VOL. VIII 1905

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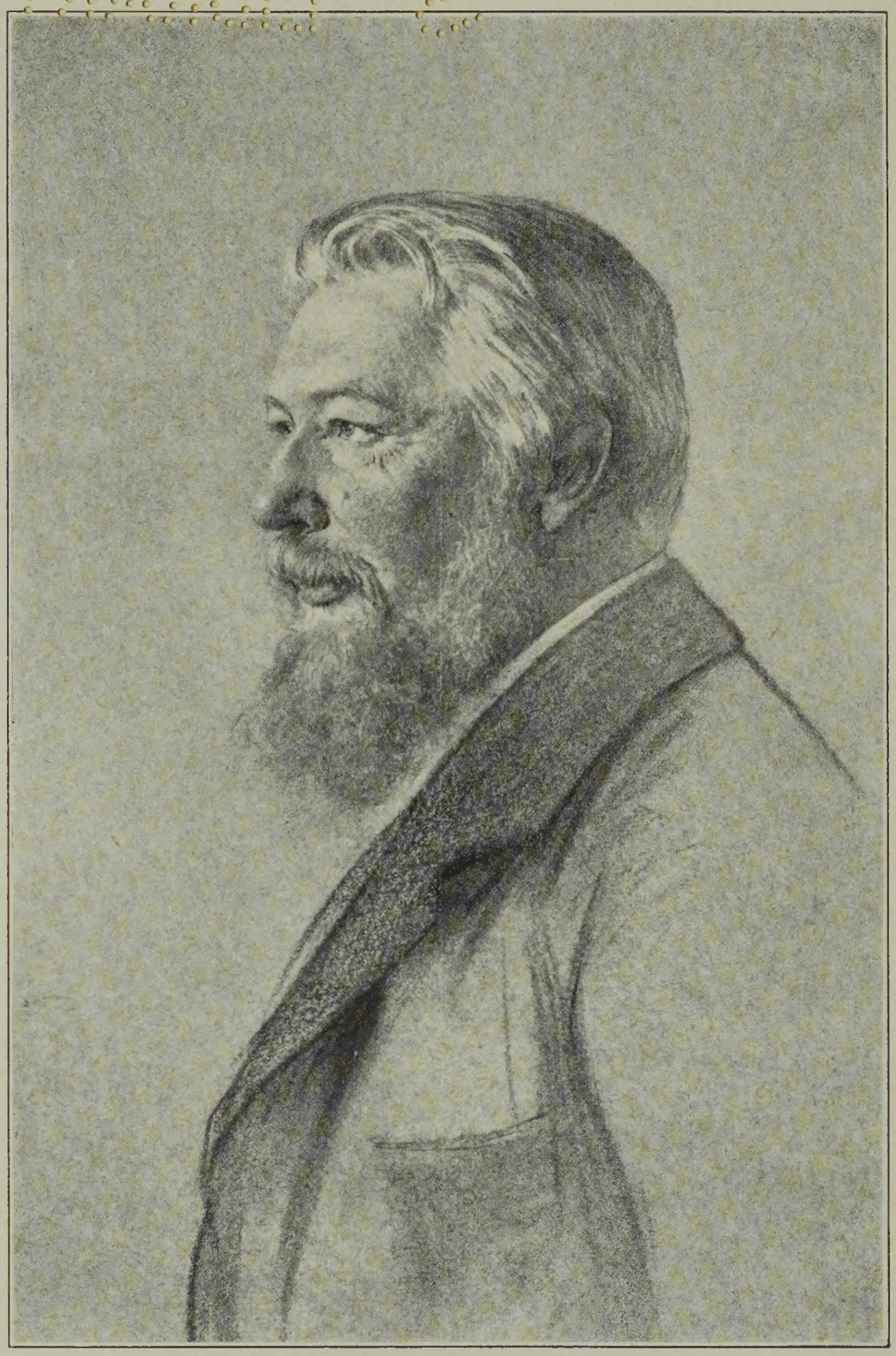

Prof. Dr. Wilhelm Ostwald

From a pastel portrait by Anton Klamroth, of Leipzig.

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TRANSACTIONS

OF THE

American Electrochemical Society

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VOLUME VIII

EIGHTH GENERAL MEETING

Bethlehem, Pa., Sept. 18, 19, 20, 1905

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1905

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VOLUME VIII. 1905.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE EIGHTH GENERAL MEETING OF THE SOCIETY, HELD AT BETHLEHEM, PA., SEPTEMBER 18TH, 19TH AND 20TH, 1905.

(Number of members registered, 41; guests, 9; total, 50.)

SESSION OF SEPTEMBER 18th.

DR. J. W. RICHARDS: On behalf of the Local Committee, which has had charge of organizing the meeting, I wish to welcome the members of the Society to Bethlehem, and to thank you for conferring on us the pleasure of your company.

We disclaim any responsibility for the weather; but I think every thing which has been within our power to order, we have ordered to the best of our ability, and for your comfort and convenience. I hope the three days which you spend among us will be days that you will remember with pleasure.

I will ask President Drinker, of Lehigh University, to kindly say some words to you on behalf of the University.

HENRY S. DRINKER, President of Lehigh University: It gives me pleasure, gentlemen, on behalf of our board of trustees and faculty, to welcome you here. We appreciate heartily the

honor you do us in selecting our University for your deliberations. To me, personally, it is peculiarly gratifying to feel that my first official act in assuming my new duties here should be to have the honor of welcoming your Society to my *alma mater*.

I assure you, while you are with us we will deem it our pleasure —our very great pleasure—to do everything we can to promote the convenience and profit of your Society. The freedom of Lehigh is yours; and while you are here our hearts and our hands are yours, also.

Dr. Richards: I have the pleasure of calling to the chair Professor Bancroft, President of the Society, who will respond to President Drinker's address of welcome.

Dr. W. D. Bancroft: I desire to express our great pleasure in accepting the invitation to hold our meeting here at Lehigh University. What with the University on the one hand and the great technical works on the other, you have that happy combination of education and application which we hope is one of the strong features of our own Electrochemical Society. It is also a pleasure to recall that we are indebted to Lehigh University for one of the prime movers in the founding of the Electrochemical Society, who was at the same time our first president—Dr. J. W. Richards.

I remember that at the time the Society was founded there was a good deal of discussion whether we were really a chemical society or an engineering society; and under those circumstances it seems to be doubly fortunate that we should meet here at Lehigh University where the late president was a chemist and the present one is an engineer.

The following papers were read and discussed, as printed in full in the Transactions:

Profs. W. S. Franklin and L. A. Freudenberger—"Note on Some Centrifugal Experiments with Colloidal Solutions."

Dr. W. D. Bancroft—"The Chemistry of Electrochemistry."

Mr. A. G. Betts—"The Phenomena of Metal Depositing."

In the evening the members of the Society were agreeably entertained by Dr. and Mrs. J. W. Richards at their residence. This was followed by a smoker at the Republican Club.

SESSION OF SEPTEMBER 19th, 1905.

THE PRESIDENT: I wish to call attention to two points. One is that we lose a large part of the actual value of the session if we have our papers read and printed without discussion. Speaking both for the people who are present at the meeting and for those who are not present, what the members wish to know is, what other people think about the papers. Therefore, the more discussion we can get on each paper, the more satisfactory it is both to the people here and still more to the people unfortunate enough not to be here. That is one side of it. The second point is that it would probably be more satisfactory if the authors presented a general abstract of their respective papers instead of reading the papers at length. I know we can all of us read the advance sheets to ourselves faster than the author can read the paper aloud; and if he goes through the whole paper right from beginning to end it does not produce as satisfactory an effect as it would if he gave the general outlines of the paper and let those who wanted to, follow the actual text. I rather think that most of the members have read in advance the papers in which they are actually interested.

The following papers were read and discussed, as printed in full in the Transactions:

Mr. O. P. Watts—"Notes on the Use of Aluminum as a Reducing Agent."

Mr. G. Gin—"New Gin Process for the Electrical Manufacture of Steel."

Mr. A. G. Betts—"An Electrolytic Process of Refining Silver."

Mr. F. D. Easterbrooks—"Electrical vs. Sulphuric Parting of Bullion."

Mr. M. Toch—"Insulating Paints."

Dr. R. von Foregger—"The Utilization of Active Oxygen, Chemically and Electrically Produced."

Mr. C. F. Carrier, Jr.—"Report on the Proposed Card Catalogue of Electrochemistry."

Prof. C. F. Burgess—"Some Observations on the Influence of Arsenic in Pickling Solutions."

Messrs. O. W. Brown and W. F. Oesterle—"The Electric Smelting of Zinc."

Mr. A. G. Betts—"Notes on the Electrometallurgy of Antimony."

After the morning session the members of the Society and guests were entertained in the Gymnasium for luncheon by Lehigh University, after which the members were shown through the works of the New Jersey Zinc Company and the Bethlehem Steel Company, both of which visits were very profitable and instructive.

In the evening the members and guests participated in a banquet at the Eagle Hotel.

SESSION OF SEPTEMBER 20th, 1905.

The following papers were read and discussed, as printed in full in these Transactions:

Mr. R. Threlfall—"A Standard Method of Measuring the Specific Resistance of Electrolytes."

"Report on the Electrochemical Exhibits at the Louisiana Purchase Exposition, 1904."

Profs. Franklin and Freudenberger—"Reversible and Irreversible Electrolytic Polarization."

Lawrence Addicks—"Ammeters for Electrolytic Work."

Dr. E. F. Roeber—"Thermodynamics of the Electric Incandescent Lamp." (With demonstrations.)

H. Schlundt and R. B. Moore—"The Chemical Separation of the Excited Activity of Thorium."

Mr. G. A. Roush—"The Electrolytic Preparation of Iodoform from Acetone."

Mr. G. Gin—"Note on the Electrical Resistivity of Iron and of Steels at High Temperatures."

R. B. Moore and Herman Schlundt—"Radioactivity of Some Natural Waters of Missouri."

Following this program of papers, Prof. Burgess made the following motion, which was carried unanimously:

Prof. Burgess: This has been one of our most successful meetings. This fact is due in large manner to the efforts of the Local Committee. It has been the smallest committee that has ever undertaken this task of providing for our entertainment and the conduct of our business, and at the same time it has been one of the most efficient. Our Society is greatly in debt to its members. I move, therefore, a vote of thanks to the Local Com-

mittee; to the Committee of Ladies who have co-operated with them; to the authorities of the Lehigh University for the hospitality which they have extended to us; to Professor Chandler for the use of his lecture room and laboratory equipment; also to the officials of the Bethlehem Steel Company and the gentlemen who have guided us on our visit at that works; to the officials of the New Jersey Zinc Company of Pennsylvania; and to the officials of the Dexter Portland Cement Company, for the courtesies which they have all extended to us.

President Bancroft then declared the Eighth General meeting adjourned.

After adjournment, Mr. F. F. Schuetz, showed and explained to the members a portable and inexpensive form of pyrometer, known as the Bristol Recording Pyrometer.

After luncheon some of the members accepted the invitation of the Dexter Portland Cement Works to visit their plant at Nazareth, Pa., and saw all stages of the manufacture of Portland cement from argillaceous limestone. Other members witnessed the opening exercises of Lehigh University.

PROCEEDINGS OF THE BOARD OF DIRECTORS.

ABSTRACTS FROM THE MINUTES OF THE MEETINGS OF DIRECTORS, HELD APRIL 25TH, 1905, TO SEPTEMBER 18TH, 1905.

In accordance with a resolution of June 3, 1905, a Japanese bond, bearing 6 per cent. interest, was purchased. This was done in order to secure a better rate of interest on the Society's money, although it was not expected that that amount of money would be actually saved in the course of the year.

The Board were notified that the Frenzel prize would be competed for, and the time for the competition was set at the next annual meeting, to be held in 1906.

Soon after Dr. Bancroft assumed the Presidency of the Society, a letter was sent out to obtain expressions of opinion from members, with regard to a number of points of vital importance to the Society. In accordance with a careful consideration of these letters by President Bancroft and the Board, it was decided at the

Eighth General Meeting of the Society, held in Bethlehem, September 18th to 20th, that in the future there be but one independent meeting a year, but that if desirable, a second meeting should be held in conjunction with one of the other large national societies, the time of this annual meeting to be determined at a later date.

Dr. Bancroft extended an invitation from Cornell University to hold the next annual meeting in Ithaca. It was then moved that this meeting be held beginning Tuesday, the first day of May, 1906.

It was moved and carried that the Society award the sum of $100 in 1906 to some member for carrying out research work in Electrochemistry, the member and subject to be decided upon by the Board.

MEMBERS ELECTED JUNE, 1905, TO OCTOBER, 1905.

June 3, 1905.

H. F. Lewis, Boston, Mass.; Dr. E. F. Smith, Philadelphia, Pa.; Dr. T. W. Richards, Cambridge, Mass.; Hubert Buckley, Niagara Falls, N. Y.

July 1, 1905.

Charles Butters, Berkeley, Cal.; Ralph D. Mershon, New York; Harvey L. Williams, Bristol, Tenn.; James K. Pumpelly, Indianapolis, Ind.; Clarence P. Hatter, Chicago, Ill.

August 5, 1905.

J. L. Malm, Cleveland, O.; Walter E. Holland, E. Orange, N. J.; George A. Guess, Silverton, Colo.; J. G. Leathart, Newcastle-upon-Tyne, Eng.; W. T. Rynard, New York; W. E. Winship, Ph. D., New York; C. E. Baker, Cleveland, O.

September 2, 1905.

Dr. R. von Foregger, New York; G. A Wells, Jr., New York.

October 2, 1905.

Frank F. Colcord, Maurer, N. J.; William F. Oesterle, Waukegan, Ill.; Coleman E. Nutter, Topeka, Kan.; John Meyer, Philadelphia, Pa.; Frank K. Cameron, Washington, D. C.

AMERICAN ELECTROCHEMICAL SOCIETY

DIRECTORY OF MEMBERS

January 1, 1906.

(*Members of date April 3, 1902, are charter members.*)

ACHESON, E. G. (Apr. 3, '02) Inter. Acheson Graphite Co., Niagara Falls, N. Y.
ACKER, Chas. E. (Apr. 3, '02) Acker Process Co., Niagara Falls, N. Y.
ACKER, O. E. (Apr. 4, '03) Acker Process Co., Niagara Falls, N. Y.
ADAMS, Prof. C. A. (Apr. 3, '02) Asst. Prof. of Elec. Eng., Harvard University, Cambridge, Mass.
ADAMS, Dr. Isaac (Apr. 3, '02) 1776 Massachusetts Ave., Cambridge, Mass.
ADAMSON, G. P. (Dec. 4, '02) Gen. Mgr., Baker & Adamson Chem. Co.; res. 238 Reeder St., Easton, Pa.
ADDICKS, Lawrence (Apr. 3, '02) De Lamar's Copper Refining Co., Chrome, N. J.; res. Perth Amboy, N. J.
AIKEN, Robert H. (Oct. 10, '03) Consulting Metallurgist, Winthrop Harbor, Ill.
ALBRO, A. B. (Apr. 7, '04) Chemist in Experimenting Laboratory, 510 W. 23d St.; res. 82 Morningside Ave., New York.
ALDEN, John (Apr. 3, '02) Pacific Mills, Lawrence, Mass.
ALLEN, Wyatt H. (Sept. 4, '02), Consult. Eng., 910-913 Union Trust Bldg., San Francisco, Cal.
ALLYN, R. S. (Feb. 5, '03) Lawyer, 41 Park Row; res. 174 W. 82d St., New York.
AMSTER, N. L. (Apr. 3, '02), Consult. Min. Eng., 32 Equitable Bldg., Boston, Mass.
ARDEN, Henry (Oct. 2, '02) Bancroft Bldg., San Diego, Cal.
ARMOR, James C. (Mar. 4, '05) Engineer, Nernst Lamp Co.; res. 931 Vickroy St., Pittsburgh, Pa.
ARMSTRONG, E. E. (Sept. 17, '03) Chemist, Acker Process Co., Niagara Falls, N. Y.
ARNOLD, T. Herbert (Mar. 4, '95) Cascade Bonanza Mines, Paulson, B. C.
ARTH, G. (Jan. 8, '04) Institut Chimique, rue Grandville 1, a Nancy M et M, France.
ASKENASY, Dr. Paul (June 6, '03) Jagdstr. 12, Nürnberg, Germany.
ASKEW, C. B. Apr. 3, '02) Consult. Eng., 1652 Monadnock Bldg., Chicago, Ill.
ATWOOD, Geo. F. (Apr. 3, '02) Western Electric Co., New York.
AUSTEN, Dr. Peter T., F. C. S. (Apr. 3, '02) 89 Pine St.; res. 204 W. 86th St., New York.
AYLSWORTH, J. W. (Mar. 5, '03) Chem. Eng. and Experimenter, Edison Storage Battery Co., 223 Midland Ave., E. Orange, N. J.
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BANCROFT, Wilder D., Ph.D. (Apr. 3, '02) Cornell University; res. 7 East Ave., Ithaca, N. Y.
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BARR, B. M. (Apr. 3, '02) 50 Lincoln St., Glen Ridge, N. J.
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BARSTOW, W. S. (Apr. 3, '02) 56-58 Pine St., New York; res. 868 Park Place, Brooklyn, N. Y.
BARTON, C. B. (Sept. 4, '02) Supt. of Electrolytic Bleach Plant, Burgess Sulphite Fibre Co., Berlin, N. H.
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BATCHELOR, Chas. (Apr. 3, '02) 52 Broadway, New York.
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BAUER, G. W. (Sept. 4, '93) Vice Pres. and Chem., Bauer, Schweitzer Hop and Malt Co., 1722 Buchanan St., San Francisco, Cal.
BAUM, I. (Dec. 3, '04) Installing Engineer, Portable Elec. Safety Light Co., Uniontown, Fayette Co., Pa.

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BISHOP, W. B. (Sept. 4, '02) Asst. Assayer, Granby Smelting, Mining and Power Co., Grand Forks, B. C.
BIXBY, Geo. L. (Aug. 7, '02) care of Pope Motor Car Co., Indianapolis, Ind.
BLACKMORE, Henry S. (Apr. 3, '02) 206 S. 9th Ave., Mt. Vernon, N. Y.
BLAKE, Lucien I., Ph.D. (Mar. 5, '04) Prof. of Physics and Elec. Eng., Univ. of Kansas, Lawrence, Kas.
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BOWMAN, Walker (Apr. 3, '02) 39 Cortlandt St., New York.
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BRIDGES, John S., Jr. (Dec. 2, '02) Associate Partner, Insurance, 70 Kilby St., Boston, Mass.
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BURGESS, Prof. C. F. (Apr. 3, '02) Engineering Bldg., Univ. of Wisconsin, Madison, Wis.

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RUSSIA.

Kharkov.—Piltschikoff, Prof. Nicholas, Technological Inst.

SWEDEN.

Gysinge.—Kjellin, F. A.
Hallstahammar.—Hedlund, Marten.
Mansbo (Avesta).—Carlson, Birger.
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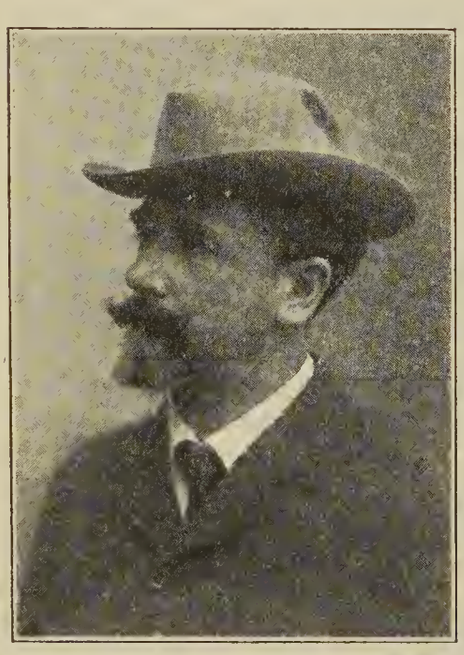


CARL KELLNER.

OBITUARY.

C. T. Child, elected April 3, 1902; died June 21, 1902.

A. B. Howard, elected April 3, 1902; died August 30, 1902.

C. W. Kennedy, elected April 3, 1902; died September 1, 1902.

H. C. Kohl, elected April 3, 1902; died November 10, 1902.

A. T. Weightman, elected April 3, 1902; died February 3, 1903.

A. Dick, elected April 16, 1903; died September 18, 1903.

F. Forbes, elected April 3, 1902; died February 18, 1904.

E. K. Adams, elected April 3, 1902; died July 21, 1904.

J. W. Best, elected July 1, 1904; died August 20, 1904.

C. M. Rosendale, elected April 2, 1903; died August 25, 1904.

E. H. Mullin, elected April 3, 1902; died January 25, 1905.

Carl Kellner, elected January 8, 1903; died June 7, 1905.

H. L. Williams, elected July 1, 1905; died July —, 1905.

157529

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 18, 1905, President Bancroft in the Chair.

THE PRECIPITATION OF COLLOIDAL SOLUTIONS BY CENTRIFUGAL FORCE. PRELIMINARY NOTE.

By W. S. Franklin and L. A. Freudenberger.

Assuming that the permanence of such colloidal solutions as those of gold, platinum and Prussian blue is due to a state of kinetic equilibrium like that of a gas, the authors have undertaken to determine the molecular weight of the colloidal substance by attempting to produce, in a centrifugal tube, an equilibrium state in which the concentration increases outwards from the axis of rotation. A clear idea of the theory of the method may be best obtained by showing its application to a gas. Thus if a tube, filled with CO_2 at 760 mm. pressure and 20°C, is placed in a centrifugal machine, the gas will settle to a state of equilibrium in which the gas will increase in density outwards from the axis, and this increase of density will be a simple function of the molecular weight of the CO_2 and of the speed. Also an ordinary solution, for example, a solution of NaCl, should, according to the ideas of solution at present held, settle in a centrifugal machine to a state of equilibrium in which the concentration increases outwards from the axis, and this increase of concentration should be a simple function of the mean molecular weight of the ultimate particles, Na (ions), Cl (ions), and NaCl (molecules), and of the speed. Similarly, a colloidal solution, if it is assumed to consist of particles held in solution by an action analogous to the commotion among the particles of a gas, should settle, in a centrifugal machine, to a state of equilibrium in which the concentration increases outwards from the axis, and this increase of concentration should be the same simple function of the molecular weight of the colloidal particles and of the speed, as in the case of a gas or in the case of an ordinary solution.

The state of equilibrium produced in a centrifugal machine should be produced also in a vessel under the action of gravity.

The variations of density in a gravity vat are, however, very small in the case of a gas, probably also in the case of an ordinary solution. In the case of a colloidal solution, on the other hand, the variation of the equilibrium density in a gravity vat would be considerable if the colloidal particles are as large as the recent work on ultra-microscopic vision seems to indicate. Therefore, it might be possible to determine the mean molecular weight of the colloidal particles by studying the equilibrium state of a colloidal solution in a gravity vat.

A very serious difficulty arises, however, in the attempt to carry out the above method for determining the molecular weight of a colloid in solution because of the excessive slowness of diffusion of the colloidal substance. Indeed, it is not known that the rate of diffusion of a colloidal substance is other than zero.

On the basis of these ideas it was thought that some indication of the feasibility of this method for determining the molecular weight of a colloidal substance could be best obtained in a centrifugal machine, not so much because the resulting differences of equilibrium density would be greater than in a gravity vat, but more especially because the great forces in a centrifugal machine would accelerate diffusion.

It may be well at this point to state the inference that may be drawn from the few centrifugal experiments, among the many that we tried, that we succeeded in performing without breaking the glass tubes by the enormous pressure of nearly 400 pounds per square inch generated in the outer ends of our tubes. The colloidal substances (platinum and Prussian blue) were precipitated in the centrifugal machine, *very much as if the earliest stages of the accelerated diffusion caused the concentration in the extreme end of the tubes next to the glass wall to be raised beyond the value at which the colloid could remain in suspension thus starting the coagulation process which swept or grew through the whole tube.*

The solutions used were (a) A brown colloidal solution of platinum, of unknown concentration, obtained by a platinum arc under distilled water, and (b) A colloidal solution of Prussian blue, $\frac{1}{27500}$ normal. Both solutions were permanent, that is, they were apparently unchanged after standing for a month in flasks.

The solutions were sealed in carefully cleaned glass tubes which were mounted in a holder on the end of the shaft of a 2 horse-power electric motor.

(a) In the case of the platinum solution the radius of rotation of the outer end of the tube was 35.9 cm., the radius of rotation of the inner end of the tube was 17.3 cm., the speed was 1,760 revolutions per minute, and all of the platinum was precipitated at the end of the tube after a run of about seven hours.

(b) In the case of the Prussian blue solution the radii were 34.0 cm., and 11.8 cm. respectively; the speed was 2,000 revolutions per minute, and all of the Prussian blue was precipitated at the end of the tube after a run of about six hours.

(a) In the case of the platinum solution the acceleration at the end of the tube was 1,244 times the acceleration of gravity, the mean acceleration along the tube was 922 times gravity, and the pressure at the outer end of the tube was about 300 pounds per square inch.

(b) In the case of the Prussian blue solution the acceleration at the end of the tube was 1,521 times the acceleration of gravity, the mean acceleration of the tube was 1,023 times gravity, and the pressure at the outer end of the tube was about 370 pounds per square inch.

These very meager results are published with some hesitation on the part of the authors, inasmuch as they realize that, in spite of the great precautions taken, the observed precipitation may have been due to some uncontrolled condition other than centrifugal action. On the other hand, difficulties of considerable magnitude were encountered before a satisfactory mounting for the tubes was devised, and many trial runs were made, only to find the apparatus broken at the end; and the authors feel on the whole justified in publishing this preliminary note.

DISCUSSION.

Dr. J. W. Richards: There are a great many things about colloidal solutions which we do not know—probably nobody knows; but the fact that the solution is precipitated by an acceleration of some thousand times gravity seems to point, in broad lines—

to prove, that the colloidal solution is a suspension, and to show that the force of gravity is not sufficient to throw down the particles; whereas, a higher acceleration is. I do not know whether that conclusion is inevitable; but it seems to me the only conclusion to be drawn from the experiment.

PROF. FRANKLIN: I do not believe that that conclusion is the only one that can be reached from the experiments. The only way that I can explain the results obtained is by assuming that at the extreme end of the tube, in some of the experiments, the centrifugal force caused a slight supersaturation, which started the coagulative process; and then the coagulate literally grew through the tube. I imagine that almost any colloid is instable when once it begins to coagulate, because of the tendency of the nucleus that is formed to gather the remainder of the dissolved substance. There was no evidence, whatever, of the formation of a stable state of equilibrium with a greater degree of concentration at one end of the tube than at the other; and this is what we were looking for in order to determine the molecular weight of the colloidal substance.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 18, 1905, Vice-President Burgess in the Chair.

THE CHEMISTRY OF ELECTROCHEMISTRY.

By Wilder D. Bancroft.

The development of electrochemistry has not been such as to lay great stress on the parallelism between electrolytic action and ordinary chemical action except for the case of the electrochemical or voltaic series. It is to the electric furnace that we really owe a new point of view. In all cases where the current is used only for heating we are, of course, dealing with the chemistry of a higher temperature pure and simple. The part played by the current is that of a glorified Bunsen burner. With this in mind we naturally ask ourselves what part is to be assigned to the current in electrolysis and how far we have to deal with any specific effect. We will define the substances carried to the anode and cathode by the current as the anions and the cations respectively. This is Faraday's definition and involves no assumptions. What the ions are in any particular case is a question to be decided by chemical analysis, using some modification of Hittorf's method. In the case of electrolysis the only specific action which we have to attribute to the current is that it tends to set free the anions at the anode and the cations at the cathode. What happens over and above that is a question of chemistry, depending on the reaction velocity and equilibrium relations in each particular case. By citing a few instances, some of them familiar to everyone, I hope to show that a closer study of the chemistry of electrochemistry will be of benefit both to chemistry and to electrochemistry.

Let us consider first the reactions at the cathode. If we pass a current through a slightly acidified solution of copper sulphate we get the precipitation of metallic copper. This is merely the normal action of the current setting free the cation, copper, at the cathode. If we acidify the solution still further, adding sulphuric acid in one case and nitric acid in another, we find that a given amount of nitric acid will prevent the precipitation of copper,

while much more sulphuric acid must be added to cause the same effect. The reason of this is clear when we consider the chemistry involved. Nitric acid attacks copper readily and sulphuric acid does not. While this is perfectly obvious when stated in this way, it has not been obvious enough in the past to induce anyone to test quantitatively the relation between the decreased current efficiency in a nitric acid solution and the rate of corrosion by that particular solution. We know that the current efficiency increases with current density,[1] which is just what we should expect if the chemical action remains constant; but more than that we do not know.

While it is only under special circumstances that it becomes impossible to precipitate copper from an aqueous solution, it is on the other hand very difficult to precipitate sodium. The rapid chemical action of sodium on water is the cause of the difficulty. If we could find a solvent which did not react with sodium and in which a sodium salt would dissolve forming a conducting solution, we should be able to precipitate sodium without difficulty. No such solvent has yet been found for sodium salts, but acetone, alcohol, pyridine, etc.,[2] are said to satisfy the condition so far as lithium salts are concerned. If we electrolyze a solution of lithium chloride in acetone, using an iron cathode, we get a bright metallic precipitate which reacts readily with water, forming lithium hydroxide. For demonstration purposes this is entirely satisfactory; but no one has ever plated lithium to any thickness, and some experiments made in my laboratory lead me to suspect that we are really dealing with a lithium-iron alloy. By working with fused salts or mixtures of fused salts we can precipitate the metals which decompose water, provided we adjust the temperature so that the precipitated metal does not react with the bath. Thus we can precipitate sodium from fused caustic soda at temperatures just above 300 degrees, but if the temperature is raised too high the sodium reacts with the bath and the yield falls off. We have a similar experience in the electrolytic precipitation of aluminum, though with different temperature limits. In the electrolysis of fused calcium or barium chloride there is a loss due to the formation of CaCl or BaCl.

Coming back to the case of a sodium salt in aqueous solution,

[1] Beadle, Electrochemist, *1*, 168 (1901).
[2] Kahlenberg. Jour. Phys. Chem. *3*, 602 (1899).
Patten and Mott. Ibid. *8*, 153 (1904).

it is easy to see that we could precipitate sodium if we could decrease the rate at which it reacts with water. Owing to the decrease of the concentration and of the vapor pressure of the sodium, sodium amalgam reacts with water much less rapidly than does metallic sodium. It should therefore be possible to form sodium amalgam electrolytically by using a mercury cathode, and this is the case. The yield depends on the relative rates of formation and decomposition of the amalgam. Sodium amalgam is less dense than mercury. If the mercury cathode is below the solution, a crust of sodium-rich amalgam forms at the surface, the rate of decomposition increases and the yield decreases. If the mercury cathode is placed above the solution by means of a porous cup or other device, the solution is in contact with a sodium-poor amalgam, the rate of decomposition is low and the yield is relatively high.[3] If we increase in any other way the rate at which sodium amalgam reacts with water we shall decrease the current efficiency. J. W. Walker[4] has shown that the presence of iron or nickel in mercury prevents the formation of sodium amalgam because the rate of decomposition becomes so high.

At low concentrations sodium amalgam is a liquid alloy, but the same general relations will hold in all cases, and it is easy to conceive of a case in which a solid alloy would have such a high rate of decomposition that it could not be formed at all if the current density or rate of formation were low and would decompose practically as fast as formed if the current density were high. This has been realized experimentally by Haber,[5] using a caustic soda solution and a lead cathode. With a moderate current density hydrogen is set free at the cathode and there are no abnormal phenomena. With a very high current density, say five ampères per square centimeter, a sodium-lead alloy is formed which breaks down practically at once, scattering pulverulent lead through the solution in a black cloud. This same black cloud is obtained chemically if we drop into water a sodium-lead alloy rich in sodium. This disintegration of the cathode through formation and decomposition of an alloy accounts for the slow blackening of platinum cathodes when a high current density is used.

[3] Shepherd, Jour. Phys. Chem., *7*, 29 (1903).
[4] Trans. Amer. Electrochem. Soc., *3*, 185 (1903).
[5] Ibid, *2*, 189 (1902).

With platinum we have usually only a surface formation of platinum black and not a violent disintegration, as with lead; but this is probably due chiefly to the difference in the concentration of the alloy formed. The important thing to be noticed is that the phenomenon became clear only when attacked both from the chemical and the electrochemical sides.

Coming back to the case of copper sulphate and starting with a neutral solution, we find cuprous oxide mixed with the copper at the cathode. This is apparently due to hydrolysis, according to the equation

$$Cu_2SO_4 + H_2O = Cu_2O + H_2SO_4.$$

The proof rests on the chemical evidence of the formation of cuprous sulphate in acid solution by heating copper sulphate with copper, the reversible reaction being[6]

$$CuSO_4 + Cu = Cu_2SO_4.$$

In neutral solutions cuprous sulphate hydrolyzes, precipitating cuprous oxide. It has also been shown that no cuprous oxide is formed electrolytically if the solution is more than slightly acid.[7] Here again the chemical and the electrochemical investigations have gone hand in hand, to the great advantage of both. It is quite possible that we should modify our views somewhat if our chemical knowledge of the subject were more accurate. We know that basic sulphates tend to precipitate when a neutral copper sulphate solution is boiled, but we do not know whether we have in the solution of the basic salt a cation containing both copper and oxygen. Such a hypothesis seems not at all improbable when we come to solutions of the sulphates of the rare earths, and there is no question about it in the case of uranyl chloride.[8]

If we electrolyze a solution of copper sulphate plus zinc sulphate we get a precipitation of copper. The reason why no zinc can precipitate as such becomes clear when we dip a rod of zinc into a copper sulphate solution. The copper precipitates and some zinc dissolves. When no other disturbing factors occur, we find that the more rapidly one metal precipitates another from solution, the less readily will that metal be precipitated electrolytically

[6] Foerster and Seidel, Zeit. anorg. Chem., *14*, 106 (1897). Cf. Richards, Collins and Heimrod, Zeit. phys. Chem., *32*, 321 (1900).

[7] Foerster and Coffetti, Zeit. Elektrochemie, *10*, 736 (1904).

[8] Hittorf, Poggendorff's Ann., *106*, 393 (1859).

from a solution containing the two metals. Thus more care has to be taken in separating silver from copper than in separating copper from zinc or cadmium. There are some apparent exceptions to this, but a study of the chemistry involved clears up matters. In sulphate, nitrate or acetate solutions, massive aluminum or massive nickel will not precipitate copper. Under certain conditions iron will not precipitate copper. In all of these solutions copper precipitates electrolytically before these other metals. If we examine into the matter we find that while nickel, for instance, does not precipitate copper, neither does copper precipitate nickel. We are therefore not dealing with a reversible reaction, and the presumption is that the conditions are not as stated. As a matter of fact we find that the aluminum, the nickel and the iron are covered with a surface film, so that the metals do not come in direct contact with the copper sulphate solution at all. With the iron a mere scratch suffices to break the film and to cause the precipitation of copper.

In a previous paper I have shown that the physical qualities of electrolytically precipitated metals become intelligible when we consider the chemistry involved.[9] In this way we get, at any rate, a tentative theory of electroplating.

Quite another set of problems comes up when we consider the electrolytic precipitation of alloys. We know that zinc and copper form six series of solid solutions at certain temperatures, and it is not at all clear how it is that copper can be precipitated pure from a solution containing zinc. The difficulty here is that we know nothing as yet about the chemical side of the problem, about the equilibrium between brass and the sulphate solutions. What has seemed to be one of the simplest problems in electrolytic analysis, the separation of copper from zinc, is really a very puzzling one theoretically, because we know so little about the chemistry of the matter. It is not possible to discuss the results of Mylius and Fromm[10] and of Senderens[11] on the chemical precipitation of alloys, because our knowledge of alloys is still very rudimentary.

The electrolysis of a solution of the sulphates of zinc and copper

[9] Jour. Phys. Chem., *9*, 277 (1904).
[10] Ber. chem. Ges. Berlin, *27*, 630 (1894).
[11] Bull. Soc. Chim. Paris, *15*, 1241 (1894); *17*, 271 (1897).

has been discussed as a separation of copper from zinc. We may also consider the electrolysis of an acidified copper sulphate solution as a separation of copper from hydrogen. Since the copper precipitates before the hydrogen we should expect this to mean that hydrogen precipitates copper from solution. At first sight this seems not to be true. One can bubble hydrogen through a copper sulphate solution forever without precipitating any copper. We are not doing our chemical experiment under the same conditions that we used in the electrochemical experiment. In the latter the copper was precipitated at an electrode. If we place a piece of metal, preferably platinum, in a copper sulphate solution and pass in hydrogen gas we shall get a reduction by the hydrogen to metallic copper.[12] It is this apparent inertness of hydrogen gas which has led to the conception of nascent hydrogen. In all cases where we have effects due to so-called nascent hydrogen, we have a metal present and the effect is either due to the metal or can be duplicated by hydrogen gas in contact with a metal. This will come up again when we consider the effects due to the nature of the cathode. There is one point, however, which is still obscure, apparently owing to our ignorance of the chemistry involved. It requires a higher voltage to set hydrogen free at certain electrodes than at others.[13] Zinc is a metal giving a particularly high "excess voltage," as it is called. It is owing to this "excess voltage" that it is comparatively easy to precipitate zinc or cadmium from a solution which is perceptibly acid. This may be connected with the fact that pure zinc does not dissolve readily in acid solutions; but beyond that our knowledge does not go as yet. It should be kept in mind, however, that the inertness of zinc to acid, or of hydrogen to copper sulphate, is different in kind from the inertness of nickel or aluminum to copper sulphate. In the first two cases contact with platinum causes the reaction to go normally. In the last two cases contact with platinum produces no effect.

We have already seen that under certain circumstances the cathode may be disintegrated mechanically. If the cation reacts with the solution to form a new solution which attacks the cathode, the cathode may be dissolved. If we electrolyze a solution of a

[12] Neumann, Zeit. phys. Chem., *14*, 193 (1894).
[13] Caspari, Ibid. *30*, 89 (1889).

sodium salt between platinum electrodes, using a diaphragm, we shall have caustic soda and hydrogen formed at the cathode. If we repeat this experiment using a hot solution between zinc electrodes the caustic soda will attack the zinc, forming sodium zincate. While this particular case has not been studied, we have a similar one in the electrolysis of ammonium nitrate solutions with an iron cathode.[14] The iron dissolves in the ammoniacal ammonium nitrate solution. The same result can be obtained chemically by placing iron in ammonium nitrate solution to which ammonia has been added. The phenomenon is purely a chemical one and is not due to a mysterious action of the electric current.

If we electrolyze the salt of a metal which can have a varying valency we may meet special difficulties, but they all become intelligible when we consider the chemistry of the solutions. If we start with a solution of ferric sulphate or chloride we do not get metallic iron precipitated, because iron and ferric sulphate or chloride react to form the ferrous salt. Since the equilibrium is reached only when practically all the ferric salt has disappeared, it is necessary to reduce the ferric salt practically completely to ferrous salt before metallic iron can be obtained. Owing to the relative instability of chromous sulphate, metallic chromium can be obtained while there is still a great deal of chromic sulphate in the solution.[15] Cuprous sulphate is so instable at ordinary temperatures that it need not be considered except in so far as we have to deal with its decomposition products in neutral solutions. At 100 degrees a measurable amount of cupric sulphate must be reduced before metallic copper will precipitate. This amount will be greater the more thoroughly the solution is stirred; in other words, the more nearly the film of solution at the surface of the cathode corresponds in composition to the solution as a whole. When a solution contains an "ous" and an "ic" salt in equilibrium with the metal, the amount of metal precipitated per 96,600 coulombs will lie between that of the two equivalent weights if no other reaction takes place. If the concentration be kept constant and if the current density be infinitely low, the weight of metal precipitated will depend on the relative amounts of the two modifications of the metal as ion. If we postulate

[14] Kaufmann. Zeit., Elektrochemie, 7, 733 (1901).
[15] Carveth. Jour. Phys. Chem. 9, 231 (1904).

Faraday's law we can determine the relative concentrations of the "ous" and the "ic" ions. Since cuprous sulphate is formed from copper and cupric sulphate with absorption of heat, it will be the more stable form at the higher temperature and the apparent equivalent weight will rise or the apparent valency decrease. This can be put in a more general form. Most salts are formed with evolution of heat and therefore tend to dissociate the higher the temperature. In general, therefore, the apparent valency of a metal will be lower the higher the temperature. At a temperature and pressure at which the silver halides decompose into silver and halogen, the valency of silver with respect to the halogen becomes zero. The same is true for mercury with respect to oxygen at the temperatures and pressures at which oxide of mercury dissociates. Reference has already been made to the existence of CaCl and BaCl at high temperatures.

For zero current density the electrochemical and the chemical equilibria must be the same for all reversible reactions. For any finite current density we have to consider reaction velocities. Massive iron does not react rapidly with a ferric salt. If the electrochemical reaction be made to take place faster than the chemical one, there may easily be a displacement of equilibrium. This applies not only to the different stages in the reduction of a metallic salt, but to the evolution of hydrogen. The percentage reduction will decrease with any change which accelerates the evolution of hydrogen. Here we have to consider both the nature and the physical state of the electrode. A depolarizer which reacts slowly will not give the same result as one that reacts rapidly, quite apart from any question of potential. In general, we can say that we shall diverge farther from the chemical equilibrium the higher the current density. This is merely another way of saying that the so-called primary reaction is favored by low current density.

We will now consider some of the reactions at the anode. The simplest case is that of a practically insoluble anode, such as graphite in a hydriodic acid solution. The normal effect of the current by definition is to set free the anion, as iodine, at the anode. This actually happens. If we electrolyze a solution containing chloride and iodide we have iodine set free. The reason that no chlorine is set free is because chlorine gas precipitates

iodine from a solution of an iodide. To this extent the reaction at the anode is the exact analogue of the reaction at the cathode. If we consider the electrolysis of hydrochloric acid between graphite electrodes we find some complications at the anode. The normal product of electrolysis is chlorine, and chlorine is the main product, under certain circumstances practically the whole product. The chlorine can and does react with the water according to the equation

$$Cl_2 + H_2O = HCl + HClO.$$

The hypochlorous acid thus formed may react in two ways,

$$3HClO = HClO_3 + 2HCl,$$

and

$$2HClO = 2HCl + O_2.$$

We will confine ourselves to the second of these reactions because it introduces another gas, oxygen. We know that this reaction takes place, but we do not know definitely whether it is or is not reversible. No one has ever made hypochlorite by the action of oxygen on sodium chloride, and this is an argument against the reaction being reversible. On the other hand Smale[16] found 0.878 volt for the electromotive force of the hydrogen-oxygen gas cell in normal hydrochloric acid; 1.074 volts for the hydrogen-oxygen gas cell in normal sulphuric acid, and 1.360 volts for the hydrogen-chlorine gas cell in normal hydrochloric acid. It is difficult to account for the low value of 0.878 volt unless one assumes, as Smale did, that the oxygen has reacted with the hydrochloric acid, setting free some chlorine. This is an argument in favor of the reaction being reversible.

If we assume that the reaction is irreversible, chemical equilibrium in the system, chlorine, hydrochloric acid and water will be reached only when all the chlorine has been replaced by oxygen. If we assume that the reaction is reversible, the chemical equilibrium will vary with the hydrochloric acid concentration, the gas phase containing a higher percentage of chlorine the more concentrated the hydrochloric acid is. On electrolysis we shall reach the chemical equilibrium if we use zero current density, and a different result with finite current densities. If the electrode has a catalytic action on hypochlorous acid, the results for any given

[16] Zeit. phys. Chem. *14*, 594 (1894); *16*, 564 (1895).

current density will come closer to the values for equilibrium than they will with an electrode which does not exert such a catalytic influence. The whole matter is complicated to a certain extent by the apparent decomposition voltage of water at 1.67 volts. While all this may appear to be hopelessly elementary, an examination of the admirable paper by Haber[17] on the electrolysis of hydrochloric acid will show that the close relation between the chemistry and the electrochemistry of the problem has not been fully understood even in the very recent past.

As has been said, the normal effect of the current on a chloride solution is to set free chlorine at the anode. If any reaction can take place more readily than the evolution of chlorine, chlorine will not be set free. If we have a zinc anode the zinc and chlorine react, forming zinc chloride, which is soluble. If we have a silver anode the silver and chlorine react, forming silver chloride, which is insoluble. Both these reactions can be duplicated chemically. If we bring caustic soda into the anode solution in any way the chlorine will react with it, forming hypochlorite as the first product. If we bubble chlorine gas into the same alkaline solution we get the same product. If we pass chlorine gas into an alkaline solution to which cobalt sulphate has been added, we get an evolution of oxygen and a precipitation of a cobaltic oxide. No hypochlorite is formed until the cobalt is oxidized completely. If we add cobalt sulphate to a sodium chloride solution and electrolyze without a diaphragm we get an evolution of oxygen at the anode and the precipitation of a cobaltic oxide. No hypochlorite is formed until the whole of the cobalt is oxidized. At ordinary temperatures this is not a catalytic reaction as has been supposed, but a coupled reaction, presumably involving the formation of an intermediate compound. It is stated on good authority that at 90 degrees the cobaltic oxide acts as a true catalytic agent. If this is true we have a most interesting change between 20 degrees and 90 degrees, one that is well worth studying and one that brings out clearly the great value of studying the chemistry of electrochemistry.

In the case of a chloride solution it was possible to isolate the normal anode decomposition product, chlorine, and to study its chemical reactions directly. This is not possible with a sulphate

[17] Zeit. anorg. Chem. *16*, 198, 329, 438 (1898).

solution because the radical SO_4 is not stable as such, or in a polymerized form, $(SO_4)n$. What is usually done is to say that this radical reacts with water, setting free oxygen according to the equation

$$2SO_4 + 2H_2O = 2H_2SO_4 + O_2.$$

This, however, is an assumption *ad hoc* and should be tested in some other way; for instance, by setting free the radical SO_4 in some purely chemical way, and showing that it does or does not react with water, setting free oxygen. This can be done by heating a solution of ammonium persulphate or of persulphuric acid. If we do this we have sulphate formed and SO_4 set free. As a matter of fact, oxygen is evolved under these circumstances.[18] If zinc or copper is placed in the solution the metal is attacked, just as it is when made anode in a sulphate solution. We thus obtain the same results by chemical methods and by electrochemical methods. It may be asked what we have gained by doing this. The justification for the point of view is the same for the sulphate electrolysis as for the chloride electrolysis, that it brings out clearly gaps in our knowledge which had hitherto been overlooked. When persulphuric acid breaks down at ordinary temperatures, the reaction proceeds in two stages, hydrogen peroxide being the intermediate decomposition product. This at once raises the question whether hydrogen peroxide is formed when a sulphate is electrolyzed. We know that hydrogen peroxide is always formed when sulphuric acid containing 60 to 90 per cent. H_2SO_4 is electrolyzed,[19] and we know that in those solutions hydrogen peroxide decomposes less rapidly than in sulphuric acid of other concentrations. It is quite conceivable that we do not detect hydrogen peroxide in other solutions merely because the catalytic action of the electrodes causes it to decompose as fast as it forms.[20] We need a careful study of the equilibrium relations and reaction velocities in the system, sulphuric acid, water and hydrogen peroxide. The chemical and electrochemical relations of ozone to these substances and to the decomposition voltage of 1.67 volts also call for a great deal of study.

[18] In showing this as a lecture experiment it is advisable to add a little manganous sulphate as catalytic agent.

[19] Richarz. Wied. Ann. *24* 183 (1885); *31*, 912 (1887).

[20] Cf. Haber and Grinberg. Zeit. anorg. Chem. *18*, 37 (1898).

One other point in regard to the electrolysis of sulphate solutions is worth noting, as it brings out clearly our ignorance. In Germany the oxygen evolved during the electrolysis of sulphuric acid is believed to come from the water, according to the equation

$$SO_4 + H_2O = H_2SO_4 + O.$$

In France the oxygen is supposed to come from the sulphate radical itself, according to the equations

$$SO_4 = SO_3 + O$$
$$SO_3 + H_2O = H_2SO_4.$$

So far as I know, no one has ever brought forward any proof which would enable us to decide between these two views. We know that solid ammonium or potassium persulphate breaks down into sulphate, sulphur trioxide and oxygen, which is an argument in favor of the French point of view. The formation of hydrogen peroxide from persulphuric acid falls more in line if we consider the oxygen as coming from the sulphate radical. On the other hand, the formation of persulphates seems to be an argument on the other side. Whatever the final decision may be, I wish now merely to emphasize the fact that this is a problem which has not been faced in the past, largely because we have kept our chemistry and our electrochemistry more or less apart.

The chemical duplication of the electrolysis of sulphate solutions was obtained by heating persulphate solutions. Addition of potassium cyanide or potassium iodide to copper sulphate solutions sets free cyanogen or iodine respectively. Mulliken[21] has shown that the same new ester is formed whether we electrolyze sodium malonic ester or whether we add iodine to the solution. A similar result could doubtless be obtained with halogen compounds by adding colloidal metals to the solution. I have not yet been able to think of any method by which we can duplicate chemically the setting free of nitrate as ion, but, of course, the percarbonate stands to the carbonate as the persulphate to the sulphate.

The oxidation of ferrous to ferric salts at the anode is merely the converse of the reduction of ferric to ferrous salts at the cathode, and therefore need not detain us. The chemical oxidation

[21] Am. Chem. Jour. *15*, 523 (1893).

of cobaltous to cobaltic sulphate needs to be studied, and the catalytic effect of hydrochloric acid on the formation of persulphuric acid will probably become intelligible when studied from the chemical side. The reason that the temperature must be kept low in the electrolytic formation of persulphates, percarbonates and cobaltic sulphate, is the very simple one that these substances decompose when heated. The essential factor is the temperature at the surface of the electrode, which is not necessarily the mean temperature of the solution[22] any more than the concentration at the surface of the electrode is necessarily the same as the mean concentration. Fischer[23] has made use of the heating of a small electrode in the experiment on the so-called disintegration of a copper anode. If a copper wire be made anode in a sulphuric acid solution while a heavy current passes, the temperature at the surface of the wire will rise and cuprous sulphate will be formed, which breaks down into copper and cupric sulphate when it is hurled by bubbles of steam out into the cold solution.

We meet another type of oxidation in the precipitation of lead peroxide during the electrolysis of acidified lead nitrate solution. This oxidation can be effected chemically by adding sodium peroxide to the solution. It is probable that this is merely an addition of concentrated hydrogen peroxide. Sodium peroxide will oxidize cobalt sulphate to cobaltic oxide, and a similar reaction can be effected electrolytically.[24]

While the reaction at the anode may be the exact converse of one at the cathode, this can be so only when the reaction in question is strictly reversible. This is very often, perhaps usually, not the case. Extreme instances are to be found in the passive metals. The reaction in the silver voltameter is sufficiently different to make it necessary to separate the anode and cathode solutions. In the formation of chlorate we always pass through the intermediate stage of hypochlorite, while this substance cannot be detected in the reduction of chlorate to chloride. One interesting case may occur when the reaction at one electrode is practically the converse of the one at the other electrode. If we electrolyze a mixture of ferric and ferrous salts between platinum

[22] Richarz and Ziegler, Wied. Ann. *63*, 261 (1897).
[23] Zeit. Elektrochemie, *9*, 507 (1903).
[24] Coehn. Ibid. *4*, 501 (1898).

electrodes, the ferrous salt will be oxidized to ferric salt at the anode and the ferric salt will be reduced to ferrous salt at the cathode. If the current densities and concentrations are so arranged that the oxidation and reduction efficiencies are each 100 per cent., and if the solution is kept well stirred, the total effect of the current will be zero[25] and the solution will behave like a metallic conductor. Metallic copper reacts with ferric sulphate, forming ferrous sulphate and cupric sulphate. If we electrolyze a solution of ferrous and copper sulphates, using a platinum anode, the ferrous salt will be oxidized at the anode, and the ferric salt thus formed will tend to react with the copper at the cathode, cutting down the current efficiency with respect to copper. If we substitute a copper anode for the platinum one, the ferrous salt cannot be oxidized, because it is easier to take copper into solution than to oxidize a ferrous salt. Consequently there will be no falling off in the cathode current efficiency.[26] If any ferric salt is formed in any other way, it will be reduced by copper from the anode rather than by copper from the cathode.

We can now take up the formation of salts. In the chlorate process we have the mixing of the cathode and the anode products, caustic potash and chlorine. The admirable work done in Foerster's laboratory has shown that there is no direct oxidation of chloride to chlorate. The success of these investigations was due primarily to the fact that Foerster and his collaborators studied the chemical and the electrochemical phenomena simultaneously. A case of theoretical interest is the electrolytic formation of hydroxides and oxides of the heavy metals. If we electrolyze a sodium chloride and a sodium sulphate solution with copper electrodes, we get an orange precipitate in the sodium chloride solution if cold, and a red one if hot, while we get a bluish precipitate in the sulphate solution if cold, and a black one if hot. The electrochemical reaction in all four cases is the formation of a copper salt at the anode and of caustic soda at the cathode, the two products then reacting. In the sulphate solution copper sulphate is formed. Now copper sulphate reacts in the cold with dilute caustic soda to form bluish cupric hydroxide. When the solutions are hot, black cupric oxide is formed. In the sodium

[25] Oettel. Zeit. Elektrochemie, *1*, 91 (1894).
[26] Bell. Jour. Phys. Chem. *7*, 652 (1903).

chloride solution, cuprous chloride is formed instead of cupric chloride. Cuprous chloride reacts with cold dilute caustic soda to form the orange-colored cuprous hydroxide, and with hot caustic soda to form red cuprous oxide. The different results in the four cases become intelligible just so soon as one considers the chemistry involved. If the same experiment is tried with nickel cathodes, the same precipitate is obtained in the four cases, but the quantity varies. There is very little difference between the two chloride solutions, but there is less precipitate in the hot sulphate solution than in the chloride solutions and there is scarcely any precipitate at all in the cold sulphate solution.[27] This fits in with what we already know as to the passivity of nickel in copper sulphate solutions. In sulphate solutions nickel becomes covered with a thin film of oxide and does not dissolve readily. In a hot solution the solvent action is greater and more nickel goes into solution to be precipitated as hydroxide by the caustic soda coming from the cathode. In chloride solutions the nickel does not become passive and very nearly the theoretical amount goes into solution.

After considering this special case of the formation of an insoluble salt we can take up the more general case. If the anion, when set free, reacts with the metal of the anode to form an insoluble salt, we shall get this salt on electrolyzing the solution, but it will be precipitated as a more or less coherent film at the anode, which may be unpleasant. If the insoluble salt can be formed away from the anode, the anode will remain bright. This happens in the electrolytic formation of the hydroxides because the insoluble salt is not precipitated until the anode and cathode solutions mix. In the Luckow patents for making insoluble salts, the solution contains two salts. The anion of one forms a soluble salt with the metal of the anode, while the anion of the second forms an insoluble salt with the metal of the anode. In making lead chromate, for instance, the salts would be sodium chlorate and sodium chromate. The object is to have the lead dissolve as chlorate and precipitate as chromate. Luckow attains this by having very little chromate relatively to sodium chlorate in the solution. It seems probable that the cell is theoretically a two-solution one without a diaphragm. If we had sodium chlorate in

[27] Le Blanc. Boltzmann's Festschrift, 183 (1904).

the anode compartment and a mixture of sodium chromate and chlorate in the cathode compartment, the formation of lead chromate would take place at the surface between the two solutions and not at the anode. If we have a single solution and a very small amount of sodium chromate, the first precipitation of lead chromate will make the concentration of sodium chromate practically zero in the immediate neighborhood of the anode. If this explanation is the correct one, vigorous stirring would be disadvantageous.

Reference has been made to the formation of an insoluble salt on the anode. This is made use of when we determine bromine or chlorine with a silver anode. The peculiarities resulting from the presence of a film on the electrode all follow from the physical and chemical characteristics of the film. In general, at the temperature of the experiment the solid salt is not a conductor of electricity. If the salt is present merely as non-conducting particles, it increases the resistance, but increases it regardless of the direction in which the current passes and regardless of the nature of the solution. This case is well illustrated by a mercury electrode covered with mercurous sulphate.[28] If the insoluble salt forms a semi-permeable membrane, we shall get added effects due to the chemical and physical peculiarities of the membrane. A copper ferrocyanide membrane is nearly impermeable to copper as ion. If we start with such a membrane in a copper sulphate solution we can precipitate metallic copper upon it by electrolysis.[29] If a membrane is impermeable to sulphate as ion and permeable to hydrogen as ion, we shall get the current passing readily in one direction while it is checked in the opposite direction. This is what appears to happen in the aluminum rectifier, and we made progress in the theory of the phenomena of the rectifier only when Taylor and Inglis[30] studied the chemical as well as the electrical phenomena.

One other point calls for discussion. It has been found that electrolytic reduction takes place more readily at certain cathodes than at others, zinc, copper and tin being the best in certain cases, lead in others. It appears to be a specific action of the cathode in

[28] Cohen. Zeit. phys. Chem., *28*, 723 (1899).
[29] Ostwald, Ibid. *6*, 71 (1890). Mijers. Recueil, Trav. Pays. Bas (2) *17*, 177 (1898).
[30] Phil. Mag., [6] *5*, 300 (1903).

each case. In the Boehringer patents for reducing nitrobenzene it was stated that one could substitute a platinum cathode for a tin or a copper cathode, provided one added a tin or a copper salt to the solution.[33] It looks, therefore, as though we were really dealing with the chemical action of the pulverulent metal on the substance to be reduced, and that the current merely regenerated the reducing agent. This brings out again the importance of studying the electrochemical phenomena with special reference to the chemical phenomena. The recent work of Tafel[34] shows that some of the mysterious changes in cathode efficiencies are due to the precipitation of minute quantities of platinum, and we have long known about the disastrous effects of platinum on storage cells. In spite of the excellent work that has been done on the electrolytic reduction of nitrobenzene, the relation between the chemistry and the electrochemistry has not always been kept in mind. Mr. J. M. Bell was once good enough to tabulate and compare for me the chemical and electrochemical methods for preparing the different reduction products of nitrobenzene. The parallelism between the two was distinctly not striking, and there is still much good work to be done in this field. The recent work on iodoform and chloroform[35] shows what can be done in the way of improving yields.

In this paper I have tried to show that we get a clearer view of the subject as a whole if we consider the chemistry of electrochemistry, and that this point of view is valuable in showing us concrete instances of research work which ought to be done.

Cornell University.

DISCUSSION.

(Communicated)

Mr. J. C. Reed: The electrochemical action at the cathode is always that of a powerful reducing agent. It reduces metals from salts to the metallic state; it reduces HNO_3, H_2SO_3, H_2SO_4, and other oxidizing agents either to the de-oxidized state or to states

[33] Chilesotti, Zeit. Elektrochemie, *7*, 768 (1901).
[34] Zeit. phys. Chem., *52*, 349 (1905).
[35] Teeple. Jour. Amer. Chem. Soc. *26*, 170, 536 (1904).

of lower oxidation. Certain metals, such as K, Na, Ca, Ba, Zn, are also powerful reducing agents.

In water, H_2SO_4 and many other acids we have examples of substances containing hydrogen, which is easily reduced to the free state, either by the electric current or by such other reducing agents as Na, K, Ba, etc.

When we pass a current through dilute H_2SO_4 between chemically inactive electrodes, we easily obtain a reduction and liberation of H by the action of the current. If we add now to the electrolyte a solution of NaCl, or Na_2SO_4, while the current is flowing, the evolution of H continues. But according to the theory explained and illustrated by Dr. Bancroft the source of the reduced H is now entirely different. The current can no longer reduce H from the electrolyte after we have added a sodium salt. While there is to all appearances no change in the action of the current—no experimental evidence of a different reaction, yet according to this theory the current ceases reducing H the instant a molecule of NaCl falls into the electrolyte. From that time on the current ignores the easily reducible H and busies itself entirely in reducing the more difficultly reducible substance Na, and this substance, after its liberation gives its attention to the work of reducing H. Dr. Bancroft has told you that it is because of this activity of sodium in subsequently reducing H that we finally obtain less sodium than corresponds to the total current. But we are to understand that the current does not reduce directly any H if there is present a more difficultly reducible substance. In other words, the electrolytic current has a peculiar preference for performing the most difficult reactions.

This theory appears to help out to a certain extent certain other similar theories, and my only objection to it is the entire absence of any experimental evidence in support of it, and the abundant evidence against it.

Until some evidence is produced in favor of this theory, I prefer the supposition which requires the least assumption, namely, that the current reduces the available conducting substance which is most easily reduced, as long as it is available in quantity sufficient to transmit the total current. If the current be increased beyond what can be transmitted by this substance, the excess of

current is transmitted by the available substance having the next higher electromotive force of decomposition.

In support of this we may cite the following facts: Copper under certain conditions is deposited from a sulphate solution with 1.22 volts and all higher potential differences, hydrogen under the same conditions, with 1.5 volts, and all higher voltages; zinc, with 2.3 volts and all higher voltages, and sodium with 4.1 volts and all higher voltages, and these decompositions occur in the same order and with the same potential differences, whether one or several of the various substances are present. The presence of Na, for example, does not change the voltage required to deposit Cu, Zn, or any other substance. If there is any reason to suppose that Na, if present, is reduced before H, the same reasons would apply to zinc if it were present. But on what grounds can we assume that Na is reduced at a less potential difference than that required by its chemical energy? The only argument on this point I have ever heard is that the Na in subsequently decomposing H_2O gives back to the current this excess of energy. But this could only be true if we assume that the current finally leaves the electrolyte through the H ion and not through the Na ion, since this must, in that case, be the ion which finally transmits the current. If this is the supposition, it is equivalent to saying that the sodium ion *is not* deposited at all, but merely acts as an intermediate link in the chain of conductors through which the current passes.

Let us see how this theory applies to the cases cited by Dr. Bancroft.

In his first illustration he says the addition of an excess of nitric acid to a solution of coper sulphate prevents the precipitation of copper, while the addition of a much greater quantity of sulphuric acid does not prevent the precipitation of copper. He says this is because nitric acid "attacks copper readily and sulphuric acid does not." He adds "this is perfectly obvious when stated in this way," meaning that it is obvious that the copper is really deposited in the presence of the excess of nitric acid, and is then subsequently dissolved by the nitric acid. To me this is not so obvious, and I believe it would not have been so obvious to Dr. Bancroft if he had performed the experiment under proper conditions. If he had maintained a constant cur-

rent and noted the potential difference as he added successive amounts of nitric acid he would have seen that there was a decrease in the potential difference and a decrease in the amount of copper deposited until the potential difference dropped to about 1.2 volts, when the deposition of copper would cease and the entire current would be transmitted by the nitric acid, which is reduced at a lower voltage than copper, the difference being with strong nitric acid about 0.7 volt. What seems to me to be perfectly obvious in this case, therefore, is that when no nitric acid is present copper alone transmits the current out of the electrolyte. (I do not mean that copper is the only conductor which transmits the current in the mass of the electrolyte), and is the only ion liberated, because it is liberated at a smaller potential difference than H, the only other cation present. Here the deposit of copper corresponds to the total current. When a small quantity of nitric acid is added, it transmits out at the cathode a part of the current because the nitrogen of HNO_3 is reduced more easily than copper (at lower voltage). The remainder of the current only is transmitted by the copper, and the deposit is less than that corresponding to the total current for that reason. It is evident that with a small percentage of nitric acid present there would be only a few molecules in contact with the cathode at a given time, and those only could transfer the current. The reason why the sulphuric acid does not prevent the deposition of copper is that it is not decomposed except at a higher voltage than that required by the copper. As we continue to add more nitric acid to the solution, we supply a larger number of molecules available at any given time in contact with the cathode. When this number is great enough to transfer the total current the deposition of copper ceases altogether. The fact that nitric acid dissolves ("attacks") metallic copper with reduction of HNO_3 to NO, is due to the simple fact that HNO_3 is a more easily reducible substance than $Cu\ (NO_3)_2$, and when both are present in the electrolyte the HNO_3 is reduced in preference to the $Cu\ (NO_3)_2$ or $Cu\ SO_4$.

Instead of saying, therefore, that the difficulty of depositing copper in the presence of HNO_3 is due to the dissolving action of HNO_3 on copper, we should say rather that metallic copper reduces ("attacks") nitric acid because nitric acid is more easily reduced electrolytically than copper.

Dr. Bancroft's second illustration is that of the difficulty of reducing sodium in the presence of a large quantity of the much more easily reducible hydrogen. He says, "The rapid chemical action of sodium on water is the cause of this difficulty," ignoring the fact that the H is more easily reduced than the sodium and that it is reduced at a voltage at which no sodium can be reduced and at all higher voltages. Why should we not say in this case also that the reason why sodium acts very energetically in liberating H from water is that H is much more easily reduced electrolytically than sodium. Dr. Bancroft says, "if we could find a solvent which did not react with sodium and in which a sodium salt would dissolve, forming a conducting solution, we should be able to precipitate sodium without difficulty." He means by that that the deposit of sodium would correspond to the total current instead of a fraction of it. He does not mean that the sodium would deposit at a lower potential difference. Did he stop to think that if such a substance were found, it would necessarily be a substance that would not be electrolytically reduced at a voltage less than that required for the sodium. If it were reduced electrolytically at a less voltage than that required for the sodium, then it would necessarily transfer the current at a less voltage and the effect on the quantity of sodium reduced would be the same as with water.

Dr. Bancroft says, "By working with fused salts or mixtures of fused salts, we can precipitate the metals which decompose water, provided we adjust the temperature so that the precipitated metal does not react with the bath." The reason for this seems to me very obvious, namely, that in the fused bath of NaCl, for example, there is nothing else present which is more easily reducible to transfer the current and, therefore, the total current must be transferred by the sodium cation and the deposit corresponds to the total current. If it were possible for the bath at any temperature to react on the deposited metal, it would be because there was something present in the bath at that temperature which the deposited metal could reduce. If that were the case, the current would also be found capable of reducing it. He says, "In the electrolysis of fused $CaCl_2$ or $BaCl_2$ there is a loss due to the formation of CaCl or BaCl." By this he means

a loss of current or that there is less metal than corresponds to the current. The reason is that part of the current is transferred by the metal reducing it to the lower chloride instead of reducing it to the metal. As a matter of fact no Ba or Ca is reduced until after a certain concentration of the lower chlorides is obtained. This case is exactly paralleled in the electrolysis of an aqueous solution of ferric chloride. The current first reduces $Fe_2\ Cl_6$ to $FeCl_2$, and it is only when a certain concentration (for a given current) of $FeCl_2$ is in contact with the cathode that any metallic iron will be deposited.

In reverting to the deposition of sodium from aqueous solutions, Dr. Bancroft explains the comparative ease of depositing sodium in a mercury cathode by saying it is because sodium amalagam reacts much less "rapidly" with water then metallic sodium. It is not a question of "rapidity" of action, but of what reaction does take place. It is a fact that a higher potential difference is required to deposit free metallic sodium electrolytically than to deposit sodium into a cathode of mercury. This is not on account of the rapidity with which sodium or sodium amalgam reduces water, but on account of the fact that with a mercury cathode the current does not reduce sodium to the *free* metal. There is another reaction possible here which requires less energy. It is reduction to the compound $NaHg_6$. The formation heat of this substance is 21,900 calories and the reduction in required voltage is $\frac{21,900}{23,24} = .94$ volt. But even with a mercury cathode it will be found that under no circumstances can any $Na\ Hg_6$ be produced at less than about 3. volts, regardless of the quantity of Hg present.

With potassium the possible reduction is greater owing to the formation of KHg_6 the formation heat of which is 34,600 cal. or 1.47 volts.

The experiment which Dr. Bancroft generously attributes to Haber[1] of pulverizing a lead cathode in a solution containing a sodium or potassium compound, shows conclusively that there is no reduction of the alkali metal at the lower voltage which liberates hydrogen freely, because there is no pulverization of the lead under those conditions. The lead is pulverized only when the

[1] Haber; Trans. Am. Electrochem. Soc, 2, 189 (1902); Reed: Jour. Frank. Inst. April, 1895.

alloy of lead and alkali metal is formed, and this takes place only when the voltage is sufficient to reduce sodium or potassium, and much greater than that necessary to reduce H. In this case at least the liberation of H cannot be due to the reaction between sodium and water, when the voltage is less than that which deposits the alkali metal.

Passing next to the illustration of electrolyzing an aqueous mixture of copper and zinc sulphates, Dr. Bancroft says, "We find that the more rapidly (meaning the more easily) one metal precipitates another from solution, the less readily will that metal be precipitated electrolytically from a solution containing both metals." This is a very correct statement of what occurs according to the theory I have advocated but not according to that of Dr. Bancroft. It is exactly similar to the case of a mixture of a copper salt and free nitric acid, except that in the mixture of Cu and Zn solutions the copper is the substance more easily reduced, while in the mixture of HNO_3 and copper sulphate the HNO_3 is the more easily reduced.

In discussing the subject of alloys Dr. Bancroft says it is not at all clear how it is that copper can be precipitated pure from a solution containing zinc. On the theory that zinc is first precipitated and that by a subsequent reaction the zinc precipitates the copper it would certainly not be clear that pure copper could be deposited from a solution containing zinc. But when we consider the copper as being directly deposited at a voltage below that required for zinc it is very clear.

I regret that I must stop at this point, in order to give this hurriedly written argument to Mr. Hering before he takes his train for Bethlehem, otherwise I should have considered *seriatim* all of the rest of Dr. Bancroft's illustrations.

DISCUSSION.

(*Communicated after adjournment by Dr. Bancroft.*)

Dr. Bancroft: It seems to me that Mr. Reed is tilting at windmills—not meaning myself. Since the electrochemical potential is proportional to the chemical potential, one must reach the

same final result whether one speaks in terms of the one or of the other. Everyone has measured electrochemical potentials for a number of years, and I wished merely to show that it was useful to look at the matter from another point of view. The measurement of electrochemical potentials has not brought out clearly the fact that we know next to nothing about what really happens during the electrolysis of sulphuric acid solutions. While I agree with much that Mr. Reed has said, I know of no way in which it can be proved that a dilute sodium amalgam contains the compound $NaHg_6$. To the uninitiated it might also seem inconsistent to treat the liquid solution of sodium in mercury one way and the solid solution of zinc in copper another.

VICE-PRESIDENT BURGESS: Is there further discussion of this paper?

MR. CARRIER: It might be of interest to Dr. Bancroft to know that in Professor Le Blanc's laboratory the preparation of lead chromate is done with an air-stream to stir the electrolyte.

PRESIDENT BANCROFT: That does not give a very effective stirring.

MR. CARRIER: That is the method he uses and is the condition which he recommended for his own students.

MR. A. G. BETTS: As I understand it, Mr. Reed's objections are based on the supposed facts that the changes requiring the least energy always take place. They do not always do so. We have a storage battery in which it takes 1⅔ volts to decompose the solution, yet it takes 2 2-10 volts to charge the cell.

Any reactions of the material of the battery electrodes may as well be disregarded. We can consider the completely charged cell, just as well, when no further action can take place on the electrodes. When the cell becomes completely charged there will be no drop of critical voltage to 1⅔ volts, but rather a slight rise to 2¼ volts, with the only result of decomposing the water requiring less than three-fourths of the electric energy used. The change requiring the least energy, that of decomposing the water, does not take place directly, and it seems to me that in all electrolysis, the mere energy requirements of the chemical decompositions are only of secondary and accidental importance

in determining the reactions, just as in the precipitation of an insoluble salt by mixing two solutions, the energy requirements, have directly little or nothing to do with it, and the whole thing depends on the physical properties of the salt formed.

MR. CARL HERING: Mr. Betts apparently refers to the usual lead accumulator. He is very much mistaken, however, in his assumption that all that is done by the 2.2 charging voltage is the decomposition of the solution. In the first place, as every one knows, the acid of the solution is actually *formed* at each electrode during charge, which is the very reverse of the process of decomposition, and which actually *adds* voltage to the system instead of consuming it. The acid of the solution is decomposed during *discharge,* and the water during the charge. But the chief point is that the charging current produces chemical changes in the materials of the two *plates* and these are what make it take a higher voltage than that required for the decomposition of the water. Mr. Betts has entirely neglected what takes place on these plates. If a current had the choice of merely decomposing sulphuric acid between platinum electrodes, a process requiring about 1⅔ volts, or of charging an accumulator, which could be tried by connecting two such cells in parallel in a main circuit, the current would not only pass through the former, which requires the least energy, but the accumulator (if partly charged) would actually *add* current to the main current by discharging, thus making the current through the water decomposing cell actually greater than the main current. This surely shows that "the changes requiring the least energy" will take place, and that something different than the mere decomposition of water takes place in charging a lead accumulator.

I differ very decidedly with Mr. Betts in his statement that "any reactions of the material of the battery electrodes may as well be disregarded." In an energy equation this would lead to absurdities. If it were correct to do this, electrochemical perpetual motions would become possible; even more than that, it would be possible to produce inexhaustible supplies of energy. If the reactions of the materials of the plates could be disregarded, why then is the capacity of an accumulator limited by the amount of material on the plates. According to Mr. Betts' contentions, it ought to be limited by the amount of water instead; this leads

to an absurdity. Mr. Betts seems to still adhere to the now ancient idea that the action of an accumulator is that water is decomposed into oxygen and hydrogen which are stored in some mysterious way in the plates, and by recombining give off the energy again. It is now known that the action is the decomposition of the sulphate of lead (or allied compounds) on the electrodes, the re-formation of which gives back the energy.

There is absolutely no reason why there should be a "drop of critical voltage to 1⅔ volts" in a charged accumulator, as he contends. The energy of a charged accumulator resides partly in the strong affinity between the spongy lead and the sulphuric acid; also in part in the less strong affinity between the peroxide of lead and the sulphuric acid; or more briefly, it resides in the affinities between the materials of the electrodes and the solution, just as in any primary battery (in most of which, however, only one plate, generally the anode, adds to the useful voltage, while the other deducts from it). It would be quite as absurd to "disregard" the reactions of the zinc anode in a primary battery, as to disregard the reactions of the spongy lead plate in an accumulator. As the energy in an accumulator resides in the affinity between the electrodes and the acid, and not in the decomposition of water, as Mr. Betts supposes, there is no reason why there should be a "drop of critical voltage" of a charged accumulator to that for the decomposition of water; it should drop merely to that voltage which corresponds to the algebraic sum of the energies of *all* the reactions.

Mr. Betts' statement that "in all electrolysis the mere energy requirements of the chemical decompositions are only of secondary and accidental (sic) importance in determining the reactions," I differ with most decidedly. An electrochemical engineer holding those views will be likely to be led into many impossible schemes and will often be sorely disappointed in finding that it takes much more energy to carry out an electrochemical process than he imagined it would. Such views would lead to electrochemical perpetual motions, just as some fifty years ago, before the principles of the conservation of energy were generally understood and accepted, many mechanics wasted much time and money in devising supposed perpetual motions of a mechanical nature.

Mr. Betts: Mr. Hering's remarks at the expense of electrochemical engineering about "investment of capital in schemes which are either incorrect in principle or impracticable from the energy standpoint" and "electrochemical perpetual motions" are trivial. I believe it is the experience of all electrochemists that the energy requirements are easily found for a process by a few simple measurements and a little arithmetic, very similar to the calculation of materials for chemical reaction. Mr. Hering is not the only one who can make and use these simple calculations.

The point I make, in agreement with President Bancroft's paper, is that the particular chemical change brought about by the final discharge, is not always that one of the possible changes which requires the least energy to bring it about. In the storage cell, which has excited this unfortunate discussion, the decomposition of the water is one of the possible changes, and the charging of the plates is another (or a series of changes). The latter takes place, though it is the one requiring most energy.

Calcium carbonate is precipitated by mixing sodium carbonate and calcium chloride solutions, possibly with absorption of heat energy, not because of the energy of the reaction, but because of a physical property of calcium carbonate, insolubility. A stick of wood does not take fire in the air and burn, although from energy requirements it ought, and this cannot be gotten away from by claiming that there is an impervious layer of oxide on the surface that protects the wood.

We have analogous conditions in electrochemistry, and these illustrations show the impracticability of looking at things from one point of view only, for instance, energy requirements.

Dr. Richards: In general, Mr. Reed's position agrees with the generality of reactions: that when the current is passed through an electrolyte that substance is decomposed which absorbs the least amount of energy; but there are exceptions which I do not know how to explain myself. When you decompose an electrolyte of caustic soda with a mercury cathode, you get sodium in the mercury, and an amalgam formed, with no hydrogen liberated; and yet the work which is done is much greater than that which is required to decompose water and set free hydrogen; so that that is one exceptional case.

In the decomposition of sulphides used as cathode in the Salom process, the current appears by preference to decompose the sulphide; whereas a smaller amount of energy would be absorbed if hydrogen were liberated, that is, if water were decomposed and free hydrogen liberated.

Those are exceptions, which perhaps may be regarded as proving the rule relied upon by Mr. Reed.

My own idea of an electrolyte is that we should consider it electrically as a unit—as a whole; that the current is not conducted through it by one ingredient, in passing from one pole to the other, but that it is conducted by the electrolyte as a unit, and that the ions are liberated only at the two poles. From there on, I agree very heartily with the bulk of Professor Bancroft's paper; but I cannot but regard the electrolyte as electrically a unit, and that the current sets free the ions which are liberated as one single act. In other words, that which we conveniently designate as primary and secondary reactions are—if you like to call them—simultaneous; which amounts to saying that you start with a certain thing, the electrolyte, and you end with certain things, the products of decomposition, and the steps are only one, although it is very convenient to regard them as two in analyzing the problem. My views on the chemistry of electrolysis in general agree with the views of our President, and may be found explained in detail in an article on "Secondary Reactions in Electrolysis," published in the journal of the Franklin Institute in September, 1901.

Mr. Carl Hering: I was very much interested in what Dr. Bancroft showed us; although I must confess that I take more comfort in the theory defended by Mr. Reed than in the one defended by Dr. Bancroft. It seems to me that the theory defended by Mr. Reed rests on a very rational basis, namely, on the sound principles of the laws of energy which have been found correct in other branches of science; why should they not be applied also in electrochemistry? According to those laws the current will do that which requires the least energy to do it. In solids we know the current will go through the path of least resistance; why should that not be equally true in electrochemistry, if we substitute for resistance, reactance, which includes voltages as well as resistances.

It seems to me that electrochemistry would advance more rapidly, and we would understand the subject much better, if we laid more stress on the thermochemical data than is generally done. In all those reactions, the thermic equation, or the energy equation, should balance, just as it does in thermodynamics and in mechanics. We have known for a great many years that perpetual motion is impossible: that is, there cannot be any excess of energy on either of the two sides of the energy equation; they must always balance. Why should they not be made to balance in electrochemistry also?

In some respects, however, I think Dr. Bancroft's theory of what might be called secondary reactions, is important; but I think great care should be taken to distinguish very clearly between two kinds of reactions, one of which is really primary and the other is unquestionably secondary. Take, for instance, the case of the deposition of zinc on a platinum electrode from an acid solution of zinc sulphate. There will be hydrogen evolved on that platinum electrode, but it is due to two entirely independent causes: one is that some of the current prefers to go through the more easily decomposed sulphuric acid instead of the more stable sulphate of zinc, and that current will deposit hydrogen. This, in my opinion, is a truly primary reaction. Additional hydrogen will be evolved because the zinc which has been deposited on the platinum by the rest of the current will be dissolved again, owing to a local current produced by platinum and zinc in sulphuric acid. This is unquestionably a true secondary reaction; but this reaction is entirely separate and distinct from the original electrochemical reaction which has deposited the zinc; it will go on after the current is stopped, which shows that it is independent. I therefore consider it very important, in all such reactions, to clearly distinguish between the truly primary reaction and such a true secondary reaction, which has nothing whatever to do with the original reaction produced by the original current but will go on whether there is any current flowing or not.

Vice-President Burgess: It appears to me that one of the commendable features of this paper is that it urges us to conduct our studies in the light of experiment. It tells us to study the electrolytic cell not on the basis of modern or ancient theories, but by experimental observation;—to observe the reactions that take place, both electrical and chemical, especially chemical.

To my mind it is rather unfortunate that Dr. Bancroft has not used the terms "primary" and "secondary" reactions, though it is true that we have no absolute means of separating the various reactions into these two classes. It is a convenience to assume, however, that the direct action of the current is to liberate certain materials, those materials being the ones which exist as ions in the electrolyte. The secondary products may be considered as those which are produced as a result of the primary products acting chemically upon the electrode or electrolyte or in being subjected to transformation in itself.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 18, 1905, President Bancroft in the Chair.

PHENOMENA OF METAL DEPOSITING.

By Anson Betts, Troy, N. Y.

This is a very important subject for the electrometallurgist. It affords to the curiosity hunter an attractive subject for research. For example, he will find among many patents and theoretical writings a proposal to add disinfectants to the solution to make solid depositions. This would, of course, kill the germs that would otherwise rot the deposit. And yet, back of such theories are reasons which appear to their authors as important. In passing, it may be mentioned that recently Dr. C. J. Thatcher[1] found that poisons would have a restraining action on the anodic oxidation of sulphites to dithionates. Poisons, of course, are only supposedly poisonous in relation to organic life, which latter might be said to rest on oxidation, but we see that poisons also affect other oxidations as well, so that they would hinder oxidation in the electrolytic metal bath. This is an illustration which shows that no matter how strange a theory of metal depositing may look at first, there are probably few which have not more than a grain of sense behind them. So that our subject may be as complicated as inorganic chemistry itself, but there are a number of new and old considerations of vastly preponderating importance, which I shall speak of particularly and attempt a partial explanation at least.

It is important to inquire into the causes of the various kinds of deposits that are obtained, both on theoretical grounds and with the desire to extend the scope of depositing processes, especially for metals which are deposited with difficulty or not at all, with the possibility that even sodium, calcium, aluminum, magnesium, etc., might, with a better theoretical knowledge, be obtained by the mere electrolysis of their solutions, and that metals which have useful properties of resisting corrosion, but are not deposited in solid enough form, may be formed electro-

[1] Electrochem. and Metallurgical Industry, *1904*, 453.

lytically into solid coatings. It might also be possible to extend electrolytic refining with solutions as electrolytes, to the refining of other metals than copper, lead, silver, nickel, tin, etc.

Professor Bancroft has treated this subject carefully and has given us his conclusions regarding the factors which improve and those which injure deposits, in the form of a table, but I have not seen any explanation of the underlying causes.

Colloids.—The idea that colloidal substances added to metal electrodepositing solutions will cause the separated metal to take a solid form is an old-established one. The facts are that some colloidal substances added to a solution such as lead fluosilicate, which by itself deposits a loose mass of lead particles, will cause a solid deposition, of which we have gelatine as a noteworthy example. But gum arabic and many other gums are also colloids and will not increase the solidity of the lead at all. On the other hand, what is thus true of colloids is true also of non-colloids, namely, a few non-colloids will cause a solid lead deposition, while a great many will not. As examples are pyrogallol and resorcin, the former of which is equal to gelatine, if not superior. Similar facts may be cited in silver deposition. For instance, carbon disulphide, not a colloid, has been found in recent experiments to be a good addition for silver methyl-sulphate solution. Another thing, gelatine is probably just as much a colloid in solution containing nitric acid as it is in solutions free from it, and yet the lead fluosilicate solution containing gelatine loses its power of depositing solid lead when nitric acid is added, not at once, because nitric acid in weak solution is a slow oxidizing agent, but in a relatively short time. As soon as the reducing action of the gelatine or other material is destroyed, the lead deposits in a loose form. For similar reasons, gelatine added to a lead nitrate bath containing a small amount of free acid will not give a solid deposit, although gelatine is still a colloid. Furthermore, gelatine added to a lead acetate solution in which no such oxidation is possible will not cause a solid lead deposition. The truth seems to be that it is a matter of indifference whether the chemical added is a colloid or not, and that the effect is due to some chemical action.

Reducing Agents.—An idea already advanced, not easily disposed of, is that reducing agents improve metal deposits. This is,

of course, not an explanation in any event. As an explanation it has been suggested that the modus operandi of reducing agents is to reduce basic salts or oxides to metal, on the cathodes, and thus get a homogeneous deposit. This cannot be the right explanation, for, in the first place, the reducing agents have not sufficient power to decompose lead hydrate, for example, into lead, the strength of pyrogallol being just about sufficient in acid solution to reduce cupric to cuprous salts, nor would the product of the reduction of insoluble metal compounds be solid metal in the second place. Then we have other means of preventing the formation of basic salts, for instance, free acid in the solution, and yet this is far from sufficient to make a solid deposit. If a chemical produces the result of a solid deposition by its reducing action, the addition of an active oxidizing agent to destroy the reducing agent, or to oxidize it, must prevent any further favorable action of the reducing agent. This is indeed the case.

Strength of Acid.—With lead it is undoubtedly a fact that the greater the chemical strength of the acid with which the solution is made up the better the results, excluding nitric acid on account of its oxidizing action. Lead fluosilicate gives a much solider deposit than lead acetate, even when gelatine is not added. The essential difference between acetic acid and fluosilicic acid is, for electrochemical purposes, one of strength.

Alkalinity of Base.—As a corollary to the above, a weak base, by destroying less of the acidity of the acid by neutralization, ought to have a little favorable influence on the deposits. Hydrogen is a weak basic element, and is a very good one to use in a solution depositing metals electro-negative to hydrogen. Antimony, gold and bismuth give good deposits without reducing agents, and form weak bases.

Attempted Explanation Based on the Theory of Concentration Cells.—In the discussion of Professor Bancroft's paper on the "Chemistry of Electroplating," presented at the St. Louis meeting of the Society, September, 1904, I introduced the idea that for an explanation we should look into the electromotive forces set up on the ridges and in the hollows of an electro-deposit, pointing out that the solution in the hollows would be weaker than that near the points of the deposit, and that the differences in concentration

could be expected to set up differences in electromotive force, and that the tendency to sprout would depend on the magnitude of these forces. I had made some experiments at that time which tended to show that this electromotive force would be less in a lead fluosilicate solution containing gelatine than in one without one, whence the greater tendency to fill up the hollows with the gelatine solution, and the solid deposit. There are a number of difficulties in the way of making determinations of the amounts of these electromotive forces, as the voltages to be read are quite small, amounting to a few thousandths of a volt in general, and disturbances are easily set up by slight quantities of impurities, including oxygen in the solution, so that my results are not of much accuracy, but they show undoubtedly that while the idea has a little value, it is far from being important enough to be in ordinary cases a determining factor. As an example, the electromotive force thus set up in the silver cyanide solution, giving a very solid deposit, is much greater than that set up in the silver nitrate solution, while the hypothesis requires just the opposite.

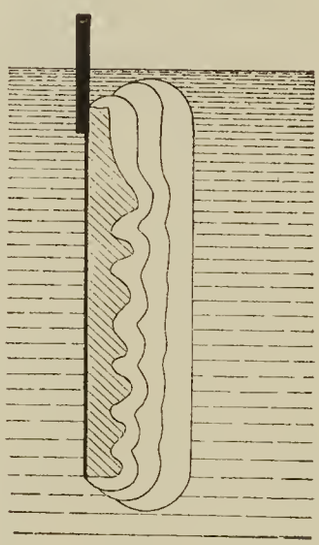


Fig. 1

If the electromotive forces thus set up (assuming their effect to be the controlling factor in determining the formation of the deposit) it is evident that if the electromotive forces of solution were approximately equal in magnitude in both the weak and strong solutions, the result would be a tendency to smooth a deposit already rough, or given a smooth surface to start on, the result would be a bright deposit. Fig. 1 illustrates this condition

of affairs, the different layers showing the gradual effect of building up all parts of the deposit at a constant rate.

On the same assumption we could have electromotive forces of the concentration cells with small positive values, that is, higher electromotive force of solution of the metal in weaker solution, and still get a solid deposit, provided the electromotive forces did not pass a certain limit, as the condition of affairs pictured in Fig. 1 is actually better than we need to have it.

Still on the same assumption, if the differences in electromotive force were great the growth might be something as shown in Fig. 2.

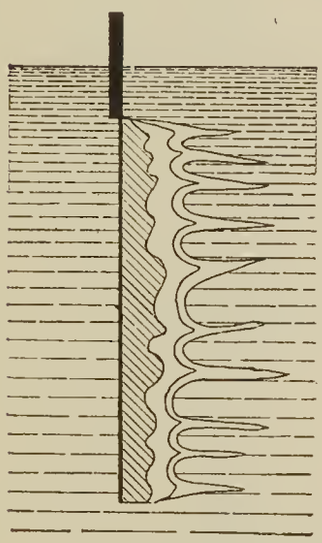


Fig. 2

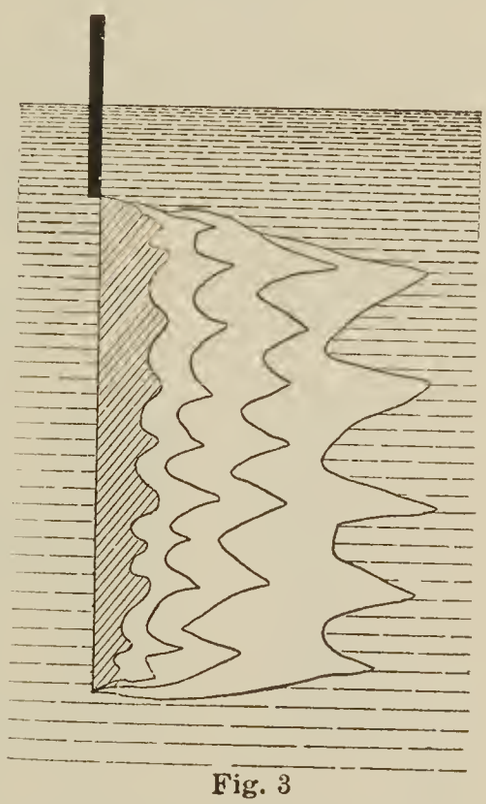


Fig. 3

With an intermediate state, allowing perhaps a speed of deposition on the points double that in the extreme deposits, the growth would probably be something as shown in Fig. 3. Antimony from the trifluoride solution has something of this appearance, and would seem to be near the critical point between branching deposits and solid deposits.

Experiment.—Small wood blocks as shown in Fig. 4 were boiled in paraffin, and pieces of paper and asbestos paper were cemented on with paraffin, asbestos being the best. The whole was then put in a beaker. The volume of catholyte inside the wood cell was about 50 cc. and the anolyte in the beaker about 250 cc., so that the e. m. fs. set up would be practically that between the

weaker cathode solution and the main body of the electrolyte, the changes in the anolyte being practically only one-fifth as great as those in the catholyte. This arrangement closely imitates the actual changes brought about near the cathode surface in electrolyzing the depositing solutions.

The different solutions used contained per litre; one-half gram-molecule of monovalent metals (silver), or one-fourth gram-molecule of divalent metals (copper and lead), and with the exception of the nitrate solutions and the silver cyanide solutions, one-half gram-molecule of free monobasic acids (acetic and

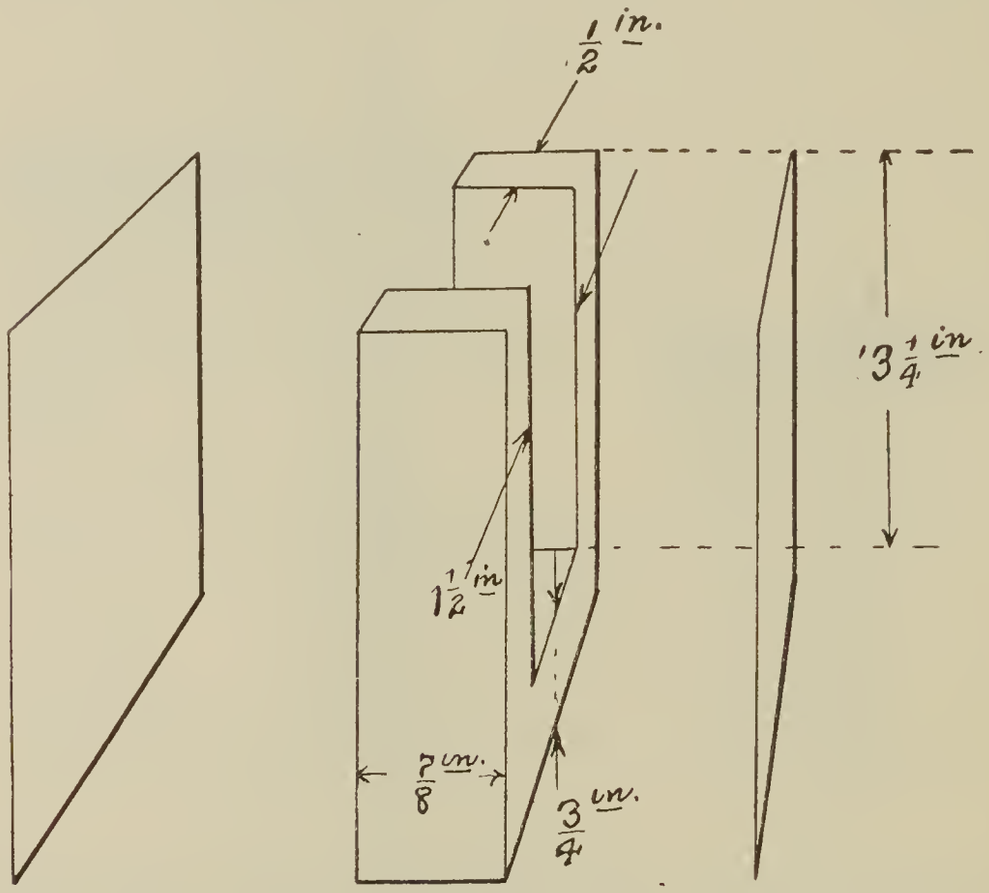


Fig. 4

methyl-sulphuric) or one-quarter gram-molecule of free dibasic acids (sulphuric and fluosilicic). The silver nitrate solution container per litre: 5 grams of nitric acid, and the lead nitrate solution contained 2.5 grams. The silver cyanide solution contained one-half gram-molecule of free potassium cyanide. Most of the results were the average of two determinations made at the same time. To deposit all the metal from 50 cc. of these solutions would require about .6 ampère hour, so that in these experiments from one-sixth to one-third of the total metal was deposited out before making the measurements. The determination of the e. m. fs.

with both smaller and greater proportions of the total metal deposited is important and remains to be done. There is a lack of agreement in some cases. For instance, a lead fluosilicate solution on the first run gave no e. m. f. at all, which I ascribe to the effect of the oxygen in the solution. With lead fluosilicate solutions which have not been in use I always notice that some lead is chemically dissolved by some oxidizer in the solution. I fear that some of the other solutions would have given somewhat different results had I had them in use long enough to get rid of dissolved oxygen. This is important to accuracy, but not in the present connection in seeking an explanation for these phenomena, for the removal of oxygen from, or the addition of it to, these solutions does not affect the character of the deposits appreciably.

The results are given in Table I:

TABLE I.

Solution	Ampere hours.	E. M F. of concentration cells.	E. M F. of concentration cells per $\frac{1}{10}$ ampere hour.	Average of number of results.
$CuSO_4$ H_2SO_4	.142	.010 volt	.007 volt	2
" "	.119	.008 "	.007 "	2
" "	.123	.008 "	.006 "	2
" "	.108	.006 "	.006 "	2
" " + gelatine . . .	.107	.006 "	.006 "	2
$PbSiF_6$ H_2SiF_6	.107	.000 "	.000 "	2
" "	.217	.006 "	.003 "	2
" "	.327	.015 "	.005 "	2
" "	.060	.003 "	.005 "	2
" "	.120	.006 "	.005 "	2
" "	.240	.011 "	.005 "	2
" " a. no gelatine	.190	.008 "	.004 "	1
" " b. gelatine in catholyte .	.190	.010 "	.005 "	1
" " a. no gelatine	.155	.013 "	.006 "	1
†" " b. gelatine in catholyte and anolyte . . .	.155	.010 "	.005 "	1
" " a. no gelatine	.222	.014 "	.006 "	1
†" " b. gelatine in both anolyte and catholyte	.222	.015 "	.007 "	1
$Pb(NO_3)_2HNO_3$	.115	.005 "	.004 "	2
†" " + gelatine .	.147	.005 "	.003 "	2
$Pb(CH_3SO_4)_2$ HCH_3SO_4 . .	.119	.008 "	.007 "	2
" " . .	.108	.007 "	.007 "	2
" " + gelatine	.107	.007 "	.007 "	2
$Pb(CH_3CO_2)_2HCH_3CO_2$ . .	.123	.004 "	.003 "	2
$AgNO_3$ HNO_3	.115	.005 "	.004 "	1
" "	.147	.008 "	.005 "	1
Ag CN KCN KCN	.107	.030 "	.028 "	1

† Gelatine in both anolyte and catholyte.

The results of this work show that the influence of the changes of concentration at the cathode are, in all cases investigated, opposed to the formation of solid deposits.

Dr. Henry J. S. Sand[2] has determined the changes of concentration at cathodes of silver, copper, platinum, etc.

High Potential Difference Between the Solution and Electrode.—This has been suggested as an explanation, but it does not explain why silver and lead, for instance, with widely different potential difference, both give, from nitrate solutions, spongy deposits, and when the potential difference for silver is made about the same as for lead, by the use of the cyanide solution, the silver separates in solid form. In the electromotive force series the metals producing good deposits and those producing bad deposits, occur in an accidental order.

Crystallization.—Metals, in common with other substances, have a tendency to crystallize, and differences in crystallization habits of the metals have been taken as an explanation of the causes of different forms of cathode growths. I quote from Roscoe and Schorlemmer's Chemistry, New York, 1900, page 63:

"Most metals, as well as their alloys, can be obtained in the crystalline state, and those occurring as minerals in the native condition are often found crystallized; this is the case with gold, silver, copper, platinum, iridium, palladium, gold-amalgam, and silver-amalgam. In general the form which they assume is one belonging to the regular system, such as the octahedron or the cube, or a combination of these forms. Some few, such as zinc, antimony, and bismuth, crystallize in the hexagonal system, and the two latter metals, which closely resemble arsenic, are found, as this is, crystallized in rhombohedra. On the other hand, a few metals, such as tin and potassium, crystallize in the quadratic system.

"To obtain metals in the crystalline state several processes can be adopted. Crystals of metals which fuse readily can be obtained by solidification after fusion. Bismuth, antimony, lead and tin may thus be crystallized, and in a similar way sodium and potassium; in the latter cases air must, of course, be excluded. Metals which are easily volatilised,[2] such as zinc, cadmium, and potassium, may be obtained in crystals by condensation from the

[2] Transactions Faraday Society, *1*, 1.

gaseous state, whilst other metals, such as silver, thallium and lead, can be readily crystallized by the electrolysis of solutions of their compounds."

We are not able to separate the metals into two groups, one of which crystallizes according to one system, and gives good deposits, perhaps, while another group crystallizes in other habits and gives non-solid deposits, and then, also, a single metal, lead being the best known example, may by apparently insignificant changes in the electrolyte, be deposited in totally different forms, so that we cannot assign to crystalline habit of a metal the controlling cause of the character of deposits made with it. It is apparent that forces are at work, or may be brought to bear, beside which the forces tending to grow large branching crystals sink into insignificance.

We have no evidence that many of our so-called crystalline deposits are crystalline at all, and especially that the external forms are crystalline. Just as a rough pile of bricks may look like crystals, but are alike in shape just because an agency has been at work making clay into similar shapes, so some agency, for example, changes in concentration, may be at work in shaping a metal deposit of similarly shaped particles. We have all seen streaked electrodeposits with vertical streaks traversing the surface, a sample of which I exhibit. If we also happened to have some other agency than the rising current at the cathode at work, only in a direction at right angles thereto and parallel to the surface, the surface would be laid off in little rectangles, which might be assumed, a few times at least, to be crystals.

Antimony deposited from the trifluoride solution has something the optical effect of changeable silk. It is built up of little pyramids with one thing in common—all the surfaces lie at an angle of about 70 degrees to the general surface. This is easily seen by holding the plate with light falling on it from different directions. In a certain direction the light is reflected from the small surfaces, making the deposit very bright, although in other positions it looks perfectly dead. The faces lie equally in all directions, but all have the same angle of elevation.

Some electrodeposits might be assumed off-hand to be crystalline, as there is a certain regularity in the appearance of the

different lumps. A solid electrolytic lead deposit under the microscope often has the appearance of rock in a quarry where trap rock or stratified rock is quarried. The stratification or cleavage of the rock often causes a certain regularity in the rock, with numerous faces in nearly parallel planes, while the actual crystallization of the rock may be on a microscopic scale.

Another thing to consider is that in first starting an electrodeposit the bare cathode must at first receive millions of crystal points of metals, while the number of lumps on the finished cathode (in metal refining) might be counted by hundreds. With a finely crystalline deposit there must be points in passing through the deposit when one crystal begins and another stops.

Experiment.—A lead cathode was marked with one horizontal scratch and three vertical scratches, and lead deposited on it from a fluosilicate solution containing gelatine. After some hours the horizontal scratch is almost invisible, while a pair of ridges extend along both sides of the vertical scratches, accentuating them. The difference in their behavior is caused, of course, by the rising current at the cathode, and shows how little influence crystalline growth has in this case, in comparison with the influence of the slight changes in density of the solution near the cathode.

Basic Salts.—It has been often said that the co-deposition of basic salts is the cause of the formation of spongy metal. This idea, at best, is only partially correct, and affords no explanation for branching deposits. I will have to cite from lead deposition again. Lead is remarkable for the great changes it is possible to make in the character of its deposits. For instance, with lead acetate solution containing free acetic acid, and lead nitrate solution containing free nitric acid, although these acids are ready solvents for basic salts, and would prevent their formation, yet the deposits are not solid at all. It is, of course, recognized that the co-deposition of basic salt may make a weak, black deposit, but it is usually easy to avoid such things merely by the proper degree of acidity.

Purity.—Purity for these considerations need be only limited to purity from metals, which, by reason of their lower e. m. f. of solution, may co-deposit with the main metal. Such impurities sometimes have a considerable effect, usually in making a

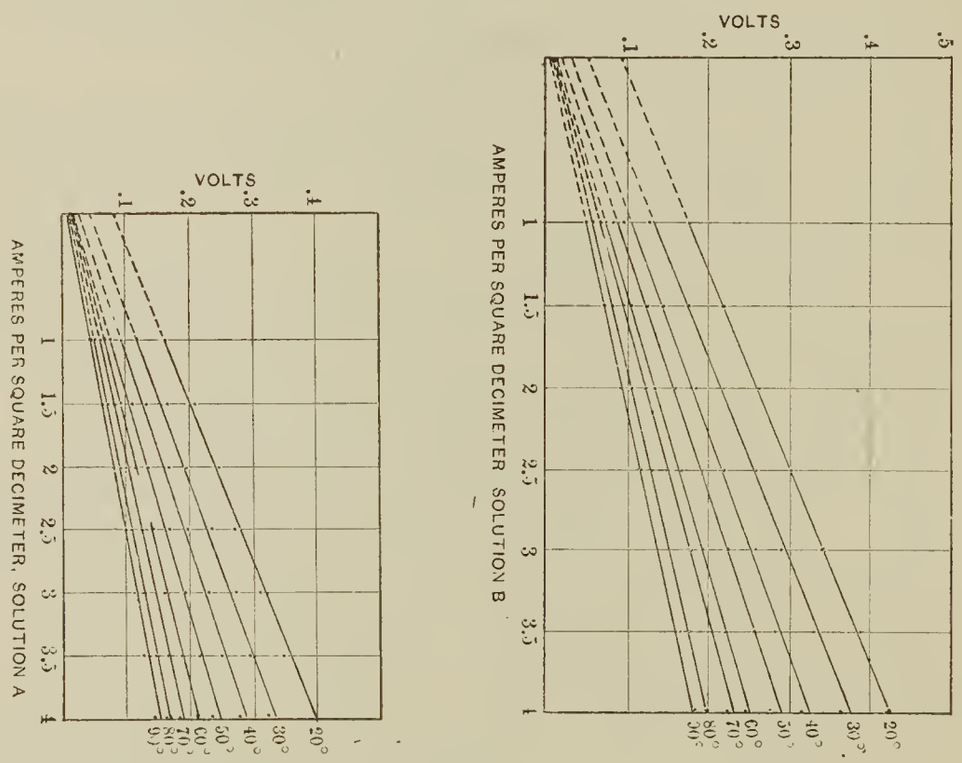
weak, black deposit, analogously to basic salts. We know that foreign conducting particles on an electrode surface usually produce lumps, and it is reasonable to suppose that the smaller the particles and the greater their number, the greater the number and the smaller the size of the resulting lumps. Furthermore, these lumps are not generally securely attached. Reducing the scale on which the phenomenon takes place tends as a result to a slimy deposit, through the stages gravelly, sandy, and gritty. If the solution contained in solution a precipitating metal as impurity the conducting particles on the surface would be very small indeed and the deposit correspondingly rotten, provided the impurity did not immediately alloy with the deposit.

Electrode Effect.—We cannot disregard the electrode itself, as it may have an influence as important, or more important, than any influence of the solution.

When we electroplate copper, lead, etc., we literally have to tear the anode metal atom from atom, and to overcome the gravitational attraction of these atoms one for another, or the tenacity of the metal, requires considerable work, which has to be done either by the current or by the heat in the electrode and solution, or by both. When the current comes to stack all these atoms up on the other electrode, if they are not put back just the way they were found there will either be an absorption or generation of thermal or electrical energy. Such a thing as this might happen: The current might deposit a layer of metal of a certain density, and when a few more layers have been applied the added pressure on the layer we first considered would compress it further. The potential energy of position would be converted into heat, so that part of the electric energy of the operation might produce heat by overcoming the resistance of the solution and part by overcoming tenacity of metal, and some of this energy might be converted to heat by such other process as I have suggested.

In Professor Bancroft's paper on "Electrolytic Copper Refining," presented before this society and contained in Vol. IV of the Transactions, page 55, we have a very complete set of measurements of voltages of copper depositing tanks. It should be noted that the voltages are not proportional to the current strength, so that we have here failure to agree with Ohm's law, and it is necessary to assume a counter electromotive force.

Referring to Professor Bancroft's Tables I and II, we may note, for example, that Solution A, with 2 ampères per square decimeter requires an electromotive force of .244 volt, and with double this density instead of the expected .488 volt only .399 volt, so that we have to assume as a consequence a counter e. m. f. of 0.089 volt. From the data given under Solution A, temperature 20 degrees, I calculated the average e. m. f. of polarization to be 0.080 volt. For the other solutions the voltages are slightly different, Solution C giving somewhat higher polarization especially.



Figs. 5 and 6

The accompanying table is calculated roughly to determine the effect of temperature in reducing the amount of this polarization. Plots of Professor Bancroft's results with Solutions A and B are given as Figures 5 and 6.

TABLE II.—SOLUTIONS A, B, C AND D.

Temp.	Polarization. Rough average, volts.
20°	0.080
30°	0.040
40°	0.025
50°	0.018
60°	0.013
70°	0.011
80°	0.010
90°	0.009

These results are plotted as Fig. 7.

The voltage thus tends to reach a limit of somewhat less than .009 volt. It would be interesting to repeat the experiments at 0° C. and 10°, and with various strengths of electrolytes.

Experiment.—Two clean copper electrodes are hung in a copper sulphate solution containing 1.63 grams of copper and 2.45 grams free sulphuric acid in 100 cc. The current passing was measured, but the record was lost. It was arranged that the current passing could be exactly doubled and tripled. Measurements were taken at intervals of several minutes.

TABLE III.

Time intervals elapsed.	Unit current.	Current doubled.	Current tripled.	Calculated polarization.
1	.080 volt	.148 volt	.203 volt	.014 volt
2	.096 "	.165 "	.223 "	.029 "
3	.105 "	.175 "	.237 "	.037 "
4	.109 "	.182 "	.237 "	.041 "
5	.112 "	.187 "	.249 "	.040 "
6	.116 "	.192 "	.254 "	.044 "
7	.120 "	.194 "	.252 "	.050 "
8	.120 "	.196 "	.256 "	.048 "
9	.123 "	.196 "	.258 "	.053 "

A little bromine was stirred into the solution, which had the effect of increasing the polarizing electromotive force to 0.078 volt.

Prof. Charles F. Burgess [3] calls attention to the polarization existing at the electrode surfaces of copper in copper sulphate plus sulphuric acid, and in copper sulphate solution without sulphuric acid, and showed that in the latter case the polarization is nearly constant with change of temperature.

This polarization has also been treated by Messrs. W. S. Franklin and L. H. Freudenberger.[4]

A similar experiment was then made with a lead fluosilicate solution of equivalent strength, containing 5.2 grams lead and 3.5 grams of fluosilicic acid per 100 cc., first without the addition of gelatine, and later with such addition, using the same current.

[3] "Notes on Economic Temperatures of Copper-Refining Solutions," Trans. Amer. Electrochemical Society, 7, 51 (1905).

[4] Ibid, p. 33.

TABLE IV.

Time intervals elapsed.	Unit Current	Current doubled.	Current tripled.	Calculated polarization.
1	.094 volt	.172 volt	.245 volt	.018 volt
2	.094 "	.172 "	.245 "	.018 "
1	.051 "	.096 "	.137 "	.007 "
1	.055 "	.104 "	.151 "	.007 "
1	.033 "	.060 "	.088 "	.006 "
5	.033 "	.060 "	.088 "	.006 "

The first two results are quite different from the rest, and should be discarded, for they were obtained while the electrodes had the fresh surface of rolled lead. All the other results, and those obtained with gelatine in the solution, below, were obtained with electrodes which had been already used.

Gelatine was added to the solution, and the following measurements were taken:

TABLE V.

Time intervals elapsed.	Unit current.	Current doubled.	Current tripled.	Calculated polarization with gelatine.
1	.100	.174	.249	.021
2	.095	.173	.249	.018
3	.088	.165	.237	.012
4	.087	.162	.235	.013
5	.086	.158	.232	.014

In making these measurements the main voltage for which I depended on my current weakened a little, accounting for the drop in current. While the measurements were rough they show that the polarization is increased by the addition of gelatine, and the solution is then a little more like the copper sulphate solution in electrode effect. It does not show the same gradual increase of polarization the copper sulphate solution does.

What becomes of the energy supplied by the electromotive force, subject to such changes with changes of temperature, equal in my experiment to something like 32 kilowatt hours per ton of copper deposited, and in Professor Bancroft's stronger

solution, at 20 degrees, to from 50 to 60 kilowatt hours? If it appears as heat the process of transformation must be different from that taking place in heating a resistance. Most of the effect seems to be a cathode effect. Is it performing some process the result of which is that the deposit is solid, whereas with lead, without this effect, the deposit is incompact?

Experiment.—In a solution of copper sulphate containing 1.63 grams copper and 2.45 grams free sulphuric acid were suspended two clean copper electrodes, area .2 sq. dm., current .116 ampère. Temperature, 21° C.

0	min.	.43 volt
5	"	.43 "
10	"	.43 "
15	"	.43 "

Reversed the current:

0	min.	.39 volt
½	"	.42 "
2	"	.42 "
5	"	.42 "

Again reversed the current:

0	min.	.42 volt
2	"	.42 "
4	"	.42 "
4½	"	.425 "
5	"	.432 "
7	"	.432 "

During the first operation copper was deposited on one plate for fifteen minutes, and then one-third of this electrolytic copper

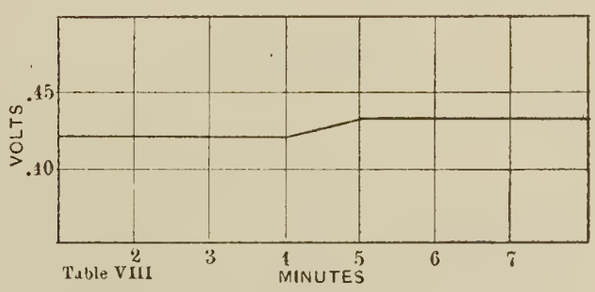


Fig. 7

was dissolved off during a reversal of the current for five minutes and deposited on the other electrode, so that both were

covered with electrolytic copper. Again after reversing, and at the end of about four and one-half minutes, when the electrolytically deposited copper is about dissolved off, the voltage took an unmistakable jump of about .01 volt, showing the electrolytic copper to contain a little more available energy than the rolled copper. The results are plotted in Fig. 7.

Metals Producing Solid and Metals Producing Branching Incompact Deposits.—A few definitions at this point are given. Electrodeposits might be roughly divided into three classes: First, smooth, tenacious deposits, which would be called good deposits; second, branching crystalline deposits, a poor deposit from the standpoint of an electro-plater and refiner because of incompactness, although the metal is pure; third, slimy non-branching deposits often called spongy, such as zinc deposits from basic solutions. It is apparent that the cause producing the third when the first or second would otherwise separate (and it is probably well understood that such things as impurity, basic salts, and low metal content are responsible), does not explain the difference between the first and second, for the third may be made in place of either of them, quite easily, and the following considerations apply to the differences of the first and second classes, being probably the least understood. This latter is also most important because it is usually easier to avoid the spongy deposit than the crystalline branching deposit. Slight changes of acidity and percentage of metal in solution are found sufficient to cause a spongy deposit to become non-slimy, but with a metal like lead, which gives a branching deposit, it takes a great deal more of investigation to find means to overcome the crystallizing tendency.

TABLE VI.

METALS PRODUCING SOLID DEPOSITS.	APPROPRIATE SOLUTIONS.
Copper	Sulphate solution, copper refining.
Zinc	Sulphate solution, electrogalvanizing.
Nickel	Sulphate solution, nickel plating.
Cobalt	Preparation of pure cobalt, Bischoff and Tiemann.

Chromium .....Chromic acid, Carveth and Curry, April meeting, A. E. S.
Iron .....Slightly acid sulphate solution, own experiments.
Antimony .....Antimony trifluoride, own experiments.
Gold .....Gold trichloride, Wohlwill's refining process.
Palladium .....Palladium ammonium chloride, Cowper-Coles process.

METALS PRODUCING LOOSE DEPOSITS

Silver .....Silver nitrate, silver voltameter.
Cadmium..... Cadmium sulphate, H. Senn, Zeitschrift f. Electrochemie, April 14, 1905.
Lead .....Lead fluosilicate, acetate, nitrate, etc.
Tin .....Tin chloride, familiar experiment for "tin tree."
Thallium .....Thallium hydroxide, Marsh's storage cell.

Hardness.—The one distinguishing feature of these two groups is their hardness.

Bottone's table of hardness, which is discredited to some extent, is given. Bottone concluded that hardness was proportional to the specific gravity divided by the atomic weight, so this is included in the table. While these figures for hardness may not be right, they are of the right order, and it is apparent that the first eight are the stronger metals, and the last four the weaker, mechanically.

TABLE VII.

Metal.	Hardness.	Specific gravity divided by atomic weight.	
Manganese	1456	.146	Good deposits.
Cobalt	1450	.141	
Nickel	1410	.150	
Iron	1375	.140	
Copper	1360	.139	
Palladium	1200	.108	
Platinum	1107	.110	
Zinc	1077	.109	
Silver	984	.0975	Intermediate in hardness.
Gold	979	.097	
Antimony	—	.056	
Bismuth	—	.047	
Cadmium	760	.077	Branching deposits.
Tin	651	.061	
Lead	570	.055	
Thallium	565	.058	

The hardness of bismuth and antimony are not given in this table, and the figures for specific gravity divided by atomic weight do not give the correct figures for hardness apparently, for antimony is unquestionably harder than lead, although the calculation gives the same figure. Bismuth is also probably harder than lead by a considerable margin. Silver and gold are reversed from the position in the scale of solidity of deposit, but there is an explanation for that, which also takes into consideration bismuth and antimony.

The tenacity of a few of these metals, taken from Ganot's Physics, translated by Atkinson, page 86, is as follows, in tenacity per sq. mm. in kilograms:

TABLE VIII.

Metal.	Drawn.	Annealed.	
Lead	2.07	1.08	Soft.
Tin	2.45	1.70	
Silver	29.00	16 2	Intermediate.
Platinum	34.10	23.50	Hard.
Copper	40.50	30.54	
Iron	61.10	46.88	

Valency.—The important influence of valency in electrochemistry is brought out, with regard to the precipitation of colloids, by Dr. W. R. Whitney in his recent paper on "Colloids,"[5] in which it is shown that the precipitating power of a salt on colloids is much greater with salts of divalent metals, and much greater still with salts of trivalent metals, than with monovalent metals, particularly with negative colloids, while with positive colloids the higher the basicity of the acid the greater the precipitating power. The table given by Dr. Whitney, as measured by Freundlich, is repeated here, but the form is changed slightly to bring this out more clearly.

TABLE IX.

ARSENIOUS SULPHIDE.		FERRIC HYDRATE.	
Salt.	*Negative.* Conc. millimol per litre.	Salt.	*Positive.* Conc. millimol per litre.
K Cl	69.	KCl	9.
KNO_3	69.8	KNO_3	11.9
Kl	67.	Kl	9.2
K_2SO_4	91.5	$Ba\ Cl_2$	9.6
$Ba\ Cl_2$	1.	K_2SO_4	0.204
$Mg\ SO_4$	1.13	$Mg\ SO_4$	0.217
$Al\ Cl_3$	0.13		
$Cr\ Cl_3$	0.13		
$Fe\ Cl_3$	0.13		

Mr. William Roy Mott, in his paper on "Colloidal Precipitation Upon Aluminum Anodes,"[6] shows this clearly. With monovalent acid radicles, as chlorides and nitrates, the colloidal aluminum hydroxide is packed down hard enough to stand a critical voltage of about one volt, rising to about 50 volts, with divalent acid radicles *(sulphates)*, and to 500 volts with trivalent salt *(citrates)*. His interesting plot of the results is repeated here as Fig. 8.

The action of these electrolytes on colloidal suspensions may cause the coherence of neighboring particles into large enough

[5] Trans. Amer. Electrochemical Society, *7*, 231 (1905).
[6] Electrochemical Industry, *2*, 445 (1904).

masses to settle from the solution. It might be that negative colloids are similar in nature to metallic ions, the difference being a vast one of size and proportionate amount of electric charge. While the effect of polyacid bases in solution will not be great enough to cause metallic ions to separate as metal masses, it may be that when metal masses are separated by other means, as by electrolysis, the effect of the basic radicle will manifest itself to at least some extent in causing the more or less firm cohesion, according to valency.

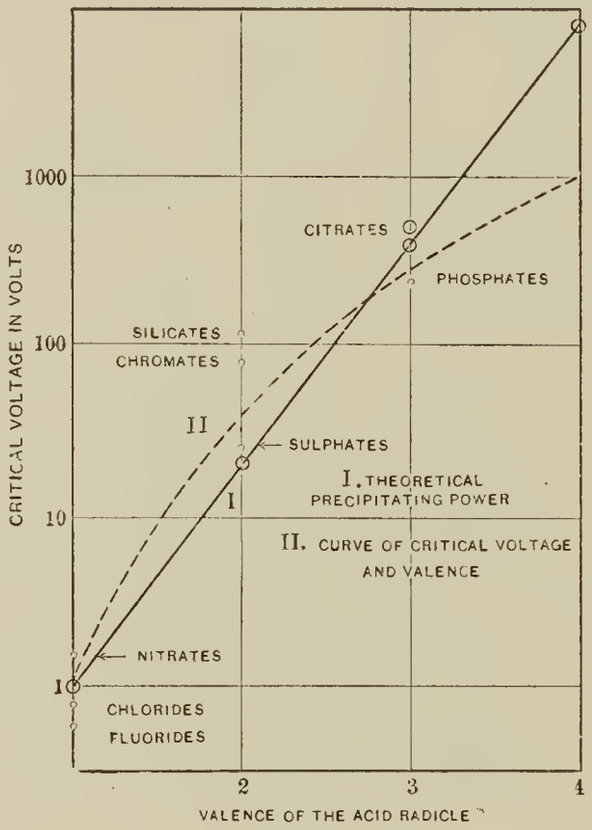


Fig. 8

When we come to that part of the scale of hardness where it is questionable whether the deposit shall be solid or not—and by hardness I do not mean particularly the resistance of the surface to scratching, but general mechanical strength—we can well believe that factors of less importance will assume a more important rôle. Monobasic silver oxide is a very strong base compared to gold trioxide, and does not give a solid deposit like gold. Bismuth and antimony are analogous to gold, and perhaps exceed it in the weakness of the basicity of their oxides.

Given the hardness of a metal (and, in case it is intermediate in the scale, its valency), it will in general now be possible to fore-

tell whether it will be deposited from aqueous solutions in non-branching form or not.

The idea now suggests itself that if our metal is not hard of itself, if we can deposit it in hard form, would it not help the solidity? I am now of the opinion that when we find a means to deposit a metal in smoother form, its principal effect is to make a harder, stronger deposit. I quote a remark from a patent on lead depositing:

"A product is easily made with a specific gravity of 11.36, the same metal remelted and cast having the same density. I prefer a current strength of 10 to 20 ampères per square foot of cathode surface. With higher current densities the lead becomes harder and more brittle and takes on a whitish color and silvery lustre. A sample deposited with a current of 40 ampères per square foot showed a specific gravity of 11.276." The point to be made is that these much harder pieces of lead (I had one piece of practically pure lead that would give a little ring when struck) are *smoother* and have a more rolling and less angular surface, and the "silvery lustre" is partly the mere optical effect of a surface without deep creases. The tensile strength of comparatively soft lead deposits is several times greater than that of rolled lead. Mr. C. T. Beilby has, however, stated in his paper on "The Hard and Soft States in Metals,"[7] that mechanically hardened silver and gold are much less translucent and more highly reflecting than the same metals are when in the soft phase, which fact was discovered by Faraday, so that the optical difference is also due to difference in hardness.

Silver deposited from the cyanide solution with the addition of carbon bisulphide added, is harder than ordinary silver and is bright; copper may be deposited from copper sulphate in varying degrees of strength and hardness by varying the composition of the solution, current density (change of concentration at cathode), and adding wood-tea, gelatine, and by varying the temperature, etc.

It takes work, of course, to harden a metal, so that we can see what becomes of the energy absorbed by the varying potential drop at cathodes. The increase of potential at the cathode in

[7] The Electrochemist and Metallurgist, 3, 811.

lead depositing is about .007 volt, when gelatine is added, as we have seen, or about 1.7 kilowatt hours per ton of lead is used to harden it.

Metals are, in general, easily hardened by drawing, rolling, hammering, and mechanical operations, and the reverse is accomplished by heat with no change in the chemical purity. These same properties of the metal may also be varied similarly by depositing them from solution under different conditions. In the deposition case it looks as though variation in chemical action caused the variations in hardness. But how? By the following considerations of the surface tension of the immersed metal—that is, the tensile strength of the successive surface layers of metal during deposition—it is seen how the variations in hardness are also in this case traceable to mechanical causes. Annealing has also, for the surface layers of a cathode, a parallel in the case of the contact of hardened metal with a suitable electrolyte, for the surface molecules may rearrange themselves, producing heat, by dissolving in the electrolyte while precipitating the equivalent amount in the stable, softer form. This affords an explanation for the fact of hardened silver giving a considerably higher *initial* electromotive force only.

Surface Tension (tensile strength).—A metal deposit is built up by the continuous addition of new surface. If the conditions on the surface are right, the deposit is bound to be right. As noted by Beilby,[8] when a metal solidifies in air, crystallization does not take place in the surface layer. To apply the same condition to a metal deposit, namely, to prevent crystallization of the surface layer, would insure that the whole deposit would be non-crystalline. For our purpose then, a consideration of surface tension is most important. It will not be taking too much for granted that materials having high cohesion, as hard metals, also have high surface tension, so that we can set the cause of variations in smoothness of metal deposits down to variations in tensile strength of the surface. The surface tension of a metal in contact with a solution is not a simple case, being a function of the cohesion of the particles of the metal, and of the cohesion of the particles of the liquid in contact with the metal, so that we must consider both.

[8] Beilby, Loc. cit.

To show that the action of surface tension is to make a deposit smooth, consider a liquid in a beaker and suppose it to have an uneven surface, as shown in Fig. 9. Surface tension will flatten it out at once independently of gravity by moving parts of the liquid bodily. Now suppose a metal deposit, as shown in Fig. 10, with a rough surface also, and to be under an electrolyte in which it may freely dissolve, and deposit from. No doubt the same forces that flatten the surface of the liquid are pulling on the metal surface trying to smooth it out, and probably they are much greater in amount than with the liquid. Yet the rigidity of the metal prevents the motion of different parts in different directions. But there is nothing to prevent this force manifesting itself to

Fig. 9

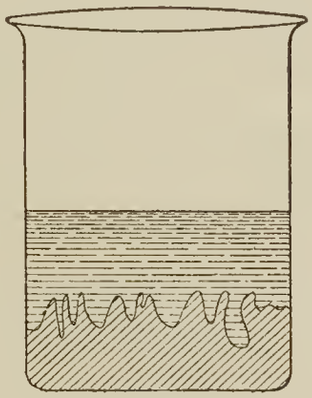


Fig. 10

influence the electromotive forces of solution in different directions, at different points, and thus setting up movements of metal *through the electrolyte* until the surface is made smooth.

There are good reasons for believing that the greater the hardness (in the general sense) of a metal the greater its surface tension, and, as a consequence, in depositing a hard metal we will have much more potent forces at work keeping the surface smooth than in depositing a soft metal. This idea agrees with the facts. The pressure, due to surface tension, will be greater, with a consequent greater compactness of metal, on the points than in the hollows, particularly when the scale of roughness is very fine, with a consequent variation of hardness, which results in variations in electromotive force. Hardened silver has an initial electromotive force of solution about .1 volt greater than ordinary silver. The heat of solution of hammered silver in mercury is 2.03 cal., + .47 cal. for annealed silver, and + .10 cal. for

crystals of electrolytic silver, as determined by Berthelot,[9] so that the hard form of metal is in a condition analogous to a compressed spring. It should be noted that these figures of Berthelot's show that ordinary electrolytic silver is *softer* than annealed silver even. When surface tension comes strongly into play the growth will not be by the application of thin layers of loose crystal masses, with projecting points forming the foundation for more points, but by the application of layer after layer of uniform thickness and non-crystalline structure, or perhaps of more finely crystalline structure, built up something as shown in Fig. 1, so that the tendency of surface tension is in general to smooth the deposit.

The objection will arise that on the scale of roughness we find on thick electrodeposits, any effect of surface tension will be too slight to have any appreciable effect. This does not appear to be really a great objection, for before roughnesses can exist on a large scale they must exist on a small scale, and going back we would reach a condition of roughness where surface tension became a controlling factor. The degree of curvature of the surfaces is then much greater and the distances between the elevated points and hollows is less, so that the effect of surface tension would increase in a geometric ratio as finer surfaces are considered. We have also noted (Fig. 1) that the application of layers of uniform thickness will tend to smooth a deposit.

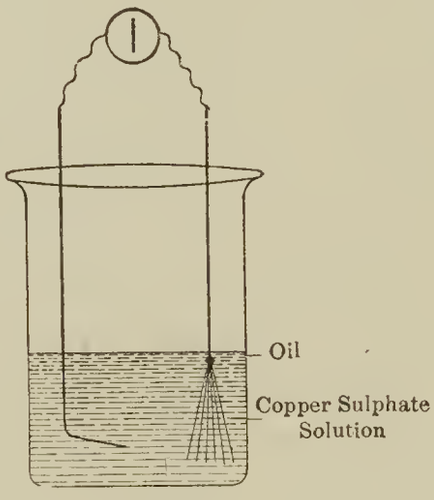


Fig 11

Experiment.—In a copper sulphate solution is dipped, as one electrode, a clean copper wire about No. 12, and as other electrode

[9] Beilby, Loc. cit., 812.

a small brush of fine copper wires, which are reduced in size to a diameter of a few thousandths of an inch by dipping in nitric acid. A little copper is then deposited on each electrode by tapping the wires leading to the electrodes with wires from a dry cell. After resting twenty minutes or so an electromotive force of about .001 volt was distinguished with a galvanometer, the direction being such that copper dissolves from the small wires and deposits on the large one. This is what would be expected from the greater convexity of the surface of the fine wires (Fig. 11). The great convexity of the small wires would put the copper under pressure by the action of surface tension.

The pressure developed, on the assumption that the surface tension of solid copper is of the same order as that of liquid mercury, and that the wires had a diameter of .1 mm., would be only about 50 grs. per sq. cm., which would be insufficient to account for any change of voltage. This experiment does not consequently prove anything, but might give a suggestion as to methods of studying these phenomena.

Relationship Between Surface Tension, Hardness, Solvent and Solubility.—That a hard metal will have a higher tensile strength in its surface than a soft one, and more particularly that a hard metal will form a surface, when deposited from solution, with a high tensile strength, seems obvious enough.

The process of dissolution is a similar one to that of evaporation, if not almost the same thing. When a salt dissolves it exerts an osmotic pressure of the same order that it would if present as a gas occupying the same space, as is well known. In the case of dissolution evaporation is made possible by the attraction of the liquid for the solid. The cohesion of the solid salt must be overcome, particularly the cohesion of the successive surface layers. It is easy to show that the greater the hardness, or cohesion, of a material, the less its solubility. As a consequence the surface tension of a salt is greater the greater its hardness. This is in agreement with the view expressed that the hard metals have a higher surface tension when immersed.

The usual explanation of surface tension is based on the gravitational effect of the molecules for each other near the plane where the transition from solid (or liquid) to air takes place.

Anything that would diminish the degree of change at this surface, *e. g.*, the substitution of a liquid for air, would diminish the cohesion of the surface layer, and it might even become negative, when the solid (or liquid) would have to dissolve. As a consequence surface tension is less for an immersed body, and the degree of change will depend on the liquid.

TABLE X.

Name.	Formula.	Hardness.	Mol. Density $\frac{\text{Sp. Gr.}}{\text{At. Wt.}}$	Solubility in one million parts water.
Diamond	C	10	.29	0
Corundum . . .	Al_2O_3	9	.040	0
Topaz	$Al(O,F_2)SiO_4$	8	.0225	0
Quartz	SiO_2	7	.0442	0
Hematite	Fe_2O_3	5.5	.0325	0
Plattnerite . . .	PbO_2	5–5.5	.0314	0
Pyrite.	FeS_2	6.–6.5	.0417	0
Hedenbergite . .	$CaFeSi_2O_6$	5.–6.–6.5	.0144	0
Acmite.	$NaFeSi_2O_6$	6.–6.5	.0152	0
Orthclase	$KAlSi_3O_8$	6.	.0093	0
Fluorspar	CaF^2	3.	.0272	12
Talc	$H_2Mg_3Si_4O_{12}$	3.5–4		?
Cryolite	Na_3AlF_6	1 –1.5	.0073	0
Calcite	$CaCO_3$	2.	.0141	Slightly sol.
Arragonite . . .	$CaCO_3$	4.	.041	0
Barite	$BaSO_4$	2.5–3.5	.0192	2.5
Celestite	$SrSO_4$	3–3.5	.0215	100
Anglesite	$PbSO_4$	2.75–3	.0202	50
Gypsum.	$CaSO_42H_2O$	1.5–2	.0135	3,000
Kieserite	$MgSO_4H_2O$	3–3.5	.0186	Insol. except by hydration.
Epsomite	$MgSO_47H_2PO$	2–2.5	.0071	724,000
Goslarite	$ZnSO_47H_2O$	2–2.5	.0070	1,400,000
Melanterite . . .	$FeSO_47H_2O$	2	.0069	500,000
Chalcancite . . .	$CuSO_45H_2O$	2	.0088	420,000
Mirabilite. . . .	$Na_2SO_410H_2O$	1.5–2	.0046	400,000
Alunogen	$Al_2(SO_4)_318H_2O$	1.5–2	.00025	1,070,000
Sylvite.	KCl	2	.0267	347,000
Halite	NaCl	2.5	.0365	360,000
Sal-Ammoniac .	NH_4Cl	1.5–2	.0285	370,000
Cerargyrite . . .	AgCl (sectile)	1–1.5	.0387	1.5
Bromyrite . . .	AgBr	2–3	.0314	.5
Sodium	Na	Very soft	.0422	Sol. in liquid ammonia without decomposition.
Ice.	H_2O	1.5	.0505	

In Table X is given a list of well-known crystalloids written down at random, numerous silicates being represented by pyroxene and orthoclase, the list containing also soluble salts occurring

crystallized in nature in a greater or less condition of purity. The figures for hardness were taken from Dana's "A System of Mineralogy," and the solubilities from Comey's "Dictionary of Solubilities." In view of the relationship between atomic density and hardness in metals, the molecular density is calculated for each crystal, and added to the table.

With the very apparent exception of such minerals as talc, mica and cerargyrite, in which cases the relationship between solubility and hardness is obscured by cleavage, etc., there is quite a remarkable agreement between solubility and hardness.

The table also includes the figures obtained by dividing the specific gravity by the molecular weight, thus giving relative figures for the number of molecules per unit volume, providing the true molecular weight is known. With the exception of the chlorides of sodium, potassium and ammonium the soluble materials in the table are those giving a figure of .0135 or less.

We have also to consider the action of the liquid in contact with the electrode as affecting the surface tension of the metal. If it were proper to speak of the hardness of a liquid, the application of a liquid of a cohesion equal to that of the metal, or say, of equal hardness, would practically do away with the causes producing a surface tension. It having been shown that the figure obtained by dividing the specific gravity by the molecular weight gives an indication, though rough, of the cohesion of a solid, we can make use of these figures for liquids.

In Table XI is given a list of liquids of importance to electrochemistry, arranged in order of molecular density. It will be seen that the so-called "ionizing" solvents stand at the head of the list, and that the solvents for extremely soft materials, as paraffin, are found at the other end.

Even a metal, metallic sodium, dissolves in liquid ammonia, and is probably also soluble in water, which would explain the violence with which it reacts with water, whereas harder aluminum does not so react.

TABLE XI.

Solvent.	Formula.	Molecular Density. $\frac{\text{Sp. Gr.}}{\text{Mol. Wt.}}$
Water	H_2O	.056
Hydrofluoric acid	HF	.050
Hydroxylamine	NH_2OH	.040
Ammonia	NH_3	.037
Nitrogen peroxide	NO_2	.034
Nitric acid	HNO_3	.0248
Hydrochloric acid	HCl	.0237
Sulphur dioxide	SO_2	.023
Carbon dioxide	CO_2	.023
Sulphuric acid	H_2SO_4	.0188
Acetic acid	$C_2H_4O_2$	.018
Alcohol	C_2H_6O	.017
Carbon disulphide	CS_2	.017
Acetone	C_3H_6O	.014
Ethyl bromide	C_2H_5Br	.014
Pyrrol	C_4H_5N	.015
Pyridine	C_5H_5N	.013
Chloroform	$CHCl_3$	.013
Titanium tetrachloride	$TiCl_4$	.0124
Phosphorous trichloride	PCl_3	.0118
Benzol	C_6H_6	.011
Normal hexane	C_6H_{14}	.008

In searching for solvents giving conducting solutions, more success is apt to be met with liquids having high molecular density.

Relationship Between Surface Tension and Valency.—This is more obscure, but I believe there is an important connection to be brought to light by researches on the precipitation of colloidal suspensions by dissolved salts.

If the dissolution depends on overcoming the cohesion of the solid, which also means that the tension of the successive surface layers is diminished, then precipitation is the result of increase of surface tension and cohesion. When a colloid is precipitated by a dissolved salt, the particles may be assumed to cohere firmly enough, one to another, to make a sufficiently large mass for gravitation to come into play, or perhaps, as appears more probable to me, the surface tension of each particle increases, and results in an enormous compression of the minute particles, to such higher specific gravity that they may drop from the solution. This view is not incompatible with the actual measurements of the

small particles of a colloidal suspension. Dr. Whitney, in his paper referred to, indicates that the diameter of the colloidal particle is about the limit of the microscopically visible, or the wave length of light, which would give them a radius of from 2 to 3.5 ten-thousandths of a millimetre. The limit of the thickness of the surface films is estimated by Quincke[10] at one ten-thousandth of a millimetre. The interior pressure of such a particle, due to surface tension, would be very great, and changes of the surface tension would affect the pressure and volume greatly. If the particle were greatly smaller still the cohesion of the particles would disappear for the most part, and it might expand directly to a gas, under the influence of the solvent, or by absorption of solvent, to a large enough volume so that surface tension could develop. There is the well-known analogy between the formation of rain drops from mist, and of coarse precipitates from fine ones, in which the effect is no doubt due to surface action in each case.

Whatever the method of operation of polyvalent radicles, it seems that it acts in affecting solids by a surface action. Surface tension and hydration of the particle may be connected. The colloidal ferric hydrate particles might have a large percentage of water squeezed out of them by an increase of surface tension brought about by the presence of a salt of a dibasic acid. On the other hand the salt of a polyacid base, ferric chloride, readily dissolves precipitated ferric hydrate and reverses the process of change of cohesion, probably also surface tension.

So does acetic acid to a greater extent, but not completely, and even more so does sulphuric, and then hydrochloric acid. Where is the transition point, when we must cease considering a physical change, and regard a chemical one?

Surface Tension of Metals Influenced by Solvents and Solutes.—In general, the surface tension of an immersed metal is less than when in the air, but will vary with various liquids, and again with various solutes. Since the molecular density of pyridine is only one-fourth that of water, which would indicate that the cohesion is less, the surface tension of lead and silver immersed in pyridine would be greater than when immersed in

[10] Carhart's Physics, *1*, 116.

water. We have Professor Kahlenberg's statements[11] that pyridine solutions of lead and silver nitrate yield solid deposits. For the simple liquids, water, alcohol, ether and carbon bisulphide the surface tension is roughly proportional to the molecular density, so the cohesion is probably about one-fourth as great for pyridine as for water. The surface tension of a number of liquids as given in Deschanel's "Natural Philosophy," translated by Everett, New York, 1894, Vol. I, p. 134, follows, in milligrammes per millimetre of length. The molecular densities, and the numbers obtained by dividing the figure for surface tension by that for molecular density, are also given for the first five liquids.

	S. T.	M. D.	$\frac{\text{S. T.}}{\text{M. D.}}$
Water, 20° C.	7.3	.056	130.
Mercury	49.1	.010	188.
Carbon bisulphide	3.57	.017	148.
Alcohol	2.5	.017	210.
Ether	1.88	.066 (?)	7440 (?)
Olive oil	3.5		
Solution marseilles soap	2.83		
Solution saporine	4.67		
Sat. sodium carbonate	4.28		
Sat. solution of camphor	4.5		

When a solvent dissolves a salt, it does so presumably because the gravitational attraction of the liquid overcomes the cohesion of the solid. A limit is reached, beyond which the solvent will dissolve no more, or is incapable of further sufficiently influencing the cohesion of the salt. Dissolved substances, in general, diminish the solvent power, and consequently the surface cohesion of the solid is greater in the solution than in the solute. If the surface tension of an immersed solid is greater in the solution than in the solvent, it follows, as a result, *dissolved substances in the solution will harden, and consequently smooth, an electrodeposit.*

Nature of Dissolved Substance.—Having reached the conclusion that dissolved substances increase the hardness, consequently the smoothness of a deposition, it will be remarked that all dissolved substances do not act in the same manner, so that we

[11] Trans. Amer. Electrochemical Society, 6, 39, 40.

should have regard to the nature of the particular substances in solution.

It has been shown that liquids having a solvent action on a solid are such that by their application to the surface of the solid the cohesion and surface tension are overcome to a great degree. As the presence of a solute in the solution in general diminishes the solvent power of the solution, so a particular solute, which by its presence prevents the solution of a particular substance, will have a greater effect in diminishing the cohesion and surface tension of this particular substance than another solute which does not so affect its solubility. When a solution is saturated with salt it has lost its power of sufficiently diminishing the cohesion of solid salt.

Also any acid has the property in solution of diminishing the solubility of salts of such acid.

Applying the same reasoning to a solid metal in contact with a solution containing a salt of the metal, the cohesion and surface tension of the metal will be diminished less than it would have been with a salt of some other metal. *Consequently a high concentration in the solution of the metal being deposited, will cause its separation in a harder and smoother form.*

As free acids and their salts have a similar effect in diminishing solubility, their effect on surface cohesion is a similar one, so that *free acids in the solution cause a harder and smoother deposition.*

It remains to be explained why acetic acid solution gives so much poorer deposits than strong acid solutions. Of course the acetates are basic salts, having basic reaction, and solutions of acetates are not much better than a colloidal solution of metallic hydroxide, a *positive* colloid. A ferric acetate solution shows the slight change from a colloidal solution, ferric hydrate separating when the solution is warm. The reason for the great difference in the action of the acids is not clear, unless it is due to the higher conductivity and greater dissociation, with the stronger acids, see "Dissociation" below.

Reducing Agents.—We have still to consider this question. It may be said that the action of gelatine is due to the fact that it is probably a poly-acid base, and may, by virtue of amide groups (NH_2) have a valency of 20 or more, so that its effect would be

due to high valency. This would not explain why pyrogallol, a simple molecule ($C_6H_6O_3$) without amido groups could do the same things as gelatine. It has been found that the addition of gelatine to a colloidal solution may change the direction of migration during electrolysis. Is this surely because it is a colloid? It seems that the effect may be due to the slow reducing action of the gelatine.

I have tried the reducing action of many inorganic reagents in lead depositing, such as chromous compounds, titanous compounds, reduction products of tungsten, molybdenum, thorium, vanadium, cerium, uranium, zirconium, sulphurous, as well as phosphorous and hypophosphorous acids, without results.

It seems that the difference lies in the very slow action of gelatine, etc., and the instantaneous action of the others. Chromous chloride, for instance, would immediately precipitate metallic copper from solution and become chromic chloride, so that any usefulness it would have would instantly disappear. Not so with gelatine which takes days to oxidize.

In other chemical operations the effect of reducing agents which do not take part in the reactions, may be far-reaching and important. It has been observed that ferric oxide (a material which when hydrated will form a colloidal solution in water) will sometimes dissolve readily in dilute sulphuric acid containing a trace of ferrous salt, but is otherwise not soluble. It seems that the solution containing the reducing agent acts to diminish the surface hardness of the *positive* material, ferric oxide, so that it may dissolve, so that we would expect a hardening effect of the reducing compound (not immediately destroyed by some chemical reaction) on a *negative* material, a metal.

Dissociation.—The theory of electrolytic dissociation does not seem to be so strongly held as it was a few years ago, but whatever causes some solutions to conduct, while others do not, be it dissociation or not, affects the properties of the solution, and would also affect the cathode surface in some way. In one case we have acetate solutions with low conductivity giving poor deposits, and with sulphate solutions, with higher conductivity, giving harder and better deposits. It is probably safe to say that *the greater the dissociation of the dissolved substance, the greater its power of aiding the hardness of the deposit.*

This is in agreement with the fact that strongly dissociating solutes produce a greater osmotic pressure than non-dissociating ones, and it is known that one dissociated molecule is as good as two undissociated ones in affecting the surface tension of the solid pure solvent (ice), so that it is not unreasonable to say that dissociated molecules will have more effect on the surface tension of immersed substances than undissociated ones.

Temperature.—With soft metals, low temperatures result in a harder deposit, for some reason, probably the following:

At low temperature solubilities are less, so the solvent has less power of overcoming surface tension and cohesion. Consequently the metals are deposited under greater surface tension at low temperatures.

With hard metals, nickel for example, the hardness is all that could be desired, and some of it could be sacrificed if a supervoltage, with less hydrogen generation, could be obtained. By raising the temperature, a softer metal is obtained, which in this case is desirable.

Surface Viscosity.—Another phenomenon, that of surface viscosity, from the action of which the surface of a liquid behaves as if it were a solid, is probably also worthy of investigation for the advancement of the metal-depositing art. It might be, that in some cases, from this cause, a *solid* layer would exist between the electrode and solution.

A concrete example of the application of the theory may be given. Take the problem of electrolytically refining iron. On referring to the table of metals on page 20 we notice that the hard metals are those that absorb hydrogen, and do not exhibit "supervoltage." An experiment shows that a good deposit of iron may be obtained while the solution is acid, but when it becomes basic, the deposit turns black. Limiting ourselves to acid solutions, if we could find a solution that would deposit soft iron, the phenomenon of supervoltage should appear, and an iron deposit might be obtained containing less hydrogen. Looking at the table of solvents we see that hydrofluoric acid has a very high molecular density, and could be depended on to soften the iron surface most. The solution should also contain quite a small amount of iron also, for the same purpose.

A test with hydrofluoric acid shows that even when hot, metallic iron dissolves very slowly, although iron rust dissolves off the iron with great speed. Fluoride solutions ought to be better than sulphate solutions for depositing iron, though they may not be good enough. The trouble with iron fluoride is that it is only slightly soluble.

The paper is incomplete and may be partly wrong, but such ideas as I have attempted to give are often found to be of great value in research, when some sort of a guide is necessary. Frequently we need such ideas, which may represent the truth only between certain limits, perhaps narrow ones; but each of such limits is often beyond the limits imposed for practical work, and in which we have interest for a particular problem.

I wish to express my great indebtedness to Prof. Charles F. Burgess, who very kindly pointed out a number of statements which would otherwise have been misunderstood, and gave me a number of valuable criticisms, so that the paper is clearer than it would have been otherwise.

DISCUSSION.

President Bancroft: Whatever may be thought of my unfortunate views on electroplating, they have at least brought the subject to the front; and I feel sure that this paper by Mr. Betts contains a great deal of material which will call for discussion.

Vice-President Burgess: I feel indebted, as I think the Society should, for the many suggestions and the various theories which Mr. Betts has given us—especially those which have been derived from his extensive and successful experience and practice in the disposition of metals.

I wish to take issue, however, with one view which he takes. If I understood it correctly, it is claimed that the tendency of metals to form crystals is not sufficiently important to be taken into account as a prominent factor in determining the quality of the deposit. It seems to me that when you get particles having similar shapes and faces which reflect the light, all of a somewhat uniform nature, those are crystals. The tendency of the circulation of the solution in altering those crystals is to round off the

corners and not make sharp crystalline points and edges. I happen to have here some microphotographs made by Dr. O. P. Watts which have a bearing upon this matter. In the deposition of iron (and by the way, I have tried to get good deposits of iron with hyrofluoric acid solutions, but have not succeeded) there is a tendency to form crystals; and their size depends on the current density, temperature, and a lot of other factors. We meet, however, smooth knobs forming on the cathode which do not appear to have any crystalline structure whatever; but to examine this further, a section of such growth was polished. A magnification of about 25 diameters revealed no crystalline structure whatever, but when subjected to much higher magnification, about 300 diameters, typical ferrite crystals were readily distinguished. I am of the belief that the majority of deposits, when examined in this way, will show a definite structure, the size and shape of the crystal being determined by the current density, temperature, and various other factors. I am not prepared to make the statement, however, that you cannot get a deposit that is not crystalline; in fact I believe it possible though not of common occurrence.

Prof. W. S. Franklin: I would like to suggest, in regard to the point brought up by Prof. Burgess, that, according to the present views in crystallography, the surface tension of a solid is what determines the elongated growths of crystals.

President Bancroft: I personally am much indebted to Mr. Betts for calling my attention to the fact that gelatine or glue possibly belongs in a class by itself, and that other colloids do not necessarily act the same way. On the other hand, I cannot quite agree with him in his classification of metals as giving good, medium and bad deposits; because you can certainly get admirable deposits of gold and silver, and of cadmium and of tin; and you can get them from the ordinary solutions. You can get practically a plating deposit of silver from a silver nitrate solution, if you want to; and one can get a beautiful deposit of tin either from stannous chloride or from sodium stannate solution; so that it seems to me that other factors are of very great importance and that it is hardly sufficient to classify metals on the basis of the way in which they act under a perfectly arbitrarily selected current density at an arbitrarily selected temperature.

As regards the question of hardness and solubility, I have an impression—subject to correction—that potassium tartrate crystals are exceedingly difficult to grind fine; that, on the other hand, they dissolve with phenomenal readiness in water; so that at least in that case there would be no direct connection between hardness and solubility.

Further, I had a feeling all through that Mr. Betts was using "surface tension" in a sense which was rather more akin to tensile strength than to the ordinarily accepted definition of surface tension. In that, of course, I may be wrong.

Dr. J. W. Richards: I wish to express my opinion of some of the points which were raised by Mr. Betts. Amongst some of the very valuable conclusions which were drawn from his experience, he has made some generalizations which I think are in many cases not warranted by even his own figures. In the question of the hardness and solubility of minerals: Professor Bancroft has just spoken of a substance which is hard and yet dissolves readily, while the tables exhibited showed some other minerals that are soft and practically insoluble. So, I think no definite conclusion at all is to be drawn and that the generalization is practically a useless one. With regard to the metals themselves, at one place Mr. Betts spoke of aluminium as a hard metal and compared it with sodium, saying that it was hard and insoluble and sodium was soft and soluble; and yet lead is almost as soft as sodium and is insoluble, so that I think many of the generalizations are misleading and practically valueless.

In considering the energy of a compressed metal—that it has less energy of solution when used as an anode because of the energy required to tear it apart—I can see that that would require work and therefore absorb energy. On the other hand, when you deposit such compressed or strong metal, it ought to take less energy to do it because of its strong condition, and yet as I understand the experiments, it took more. I would consider the powdered metal as being in a higher energy condition than a strong metal, because it takes energy to transform the strong metal into the powdered condition, and the experiment seemed to contradict that.

The question of hardness was raised by Mr. Betts, and in his tables he used Bottome's scale of hardness, which is, I think,

almost entirely unreliable. Any generalizations—even if they had been observed—based on that table would have been valueless.

Mr. Betts: Professor Burgess says that crystallization is a very important thing. While I do not deny that—I have seen too many crystalline deposits—yet I have seen crystallization overcome in the application of smooth layers which would not be crystalline layers.

Vice-President Burgess: Are not those smooth layers, simply layers of smaller crystals?

Mr. Betts: Perhaps they are. Professor Richards I think said that sodium was not much different from aluminum in solubility. Take liquid ammonia; it dissolves sodium readily enough. You cannot dissolve aluminum in it. Then President Bancroft cites potassium tartrate as very hard, but it is not so very hard, though perhaps elastic. I have never heard of its being used for drills in place of diamonds. Replying to Prof. Richards, I think he said the compressed metal would dissolve with more difficulty than metal in the soft phase. It is just the opposite, by experimental evidence. The hard metal gives off more heat when it is dissolved than the soft metal does. Also the hard phase has a higher electromotive force of solution.

Dr. Richards: I thought I had understood that the compressed metal (that is the strong metal) gave off less energy when used as anode. It certainly ought to; and *vice versa* to absorb less energy in being deposited in the compact state.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 19, 1905, President Bancroft in the Chair.

NOTES ON THE USE OF ALUMINUM AS A REDUCING AGENT.

By Oliver P. Watts.

The use of aluminum as a reducing agent is now of such importance that any extension of its field of usefulness seems worthy of record, and accordingly the writer presents a new way of using it, which yields results heretofore unattained by other methods.

The early method of adding the substance to be reduced to a bath of fused aluminum gave, in the hands of Moissan and others, only alloys. Dr. Goldschmidt, by using the aluminum as grains or powder in his now well-known method, successfully overcame the tendency of the aluminum to alloy with the reduced metal, and thus produced a long series of carbon-free metals.

There remained, however, certain metals, *e. g.*, titanium and tungsten, which could not be obtained in a pure state even by this process. Success depends upon the attainment, as a result of the chemical reaction, of a temperature so high that reaction takes place completely, and that the products are perfectly fluid. The reaction of aluminum with the oxides of titanium and tungsten fails to yield this required temperature, hence these metals cannot be obtained by the Goldschmidt process. Yet their alloys with some metal whose compounds are more easily reduced by aluminum may be thus obtained. The addition to the charge of the oxide of iron, for example, supplies the heat necessary for a complete reduction and for the agglomeration of the resulting iron alloy. In this way Dr. Goldschmidt produces ferro-titanium and ferro-tungsten.

By a modification in the method of using the fused bath of aluminum, A. J. Rossi (*Electrochem. Ind.*, 1903, Vol. I, 523) succeeded in obtaining ferro-titanium and ferro-tungsten in large quantity and free from aluminum. His method consists in melting the aluminum in an electric furnace, feeding in the mixed oxides to be reduced, and after reaction has occurred, adding an

excess of the oxides to remove the last traces of aluminum from the alloy produced.

In the absence of any statement to the contrary, the writer deems it improbable that this process, so successful in producing the ferro-metals, would yield titanium or tungsten free from aluminum. To remove all aluminum from an alloy, even at electric furnace temperatures, requires that the oxidizing agent used shall not be extremely difficult of reduction. In experiments by the writer on the reduction of fused silica and silicates in the electric furnace by adding ingot aluminum, some of the latter always remained in the silicon reduced. The large excess of fused silicate with which the product was in contact failed to remove the last traces of aluminum. It is reasonable to suppose that titanium oxide would act no more energetically than silica as an oxidizing agent.

There seems, then, to be lacking a method by which aluminum as a reducing agent may be made to yield the pure metals, titanium, tungsten, uranium and some others.

In the course of a long series of experiments, begun in 1904, on the production of metallic borides and silicides, the writer discovered that Goldschmidt charges could, by a slight change, be fired with safety in an electric furnace of the arc type. Powdered fluorspar or cryolite was added to the charge to reduce the velocity of reaction. Other inert powders could no doubt be substituted for these. The charge was placed in the cavity of a furnace with a magnesite lining, the cover put on, and an arc started just above the charge. The usual heating was for five minutes at 300 ampères and 70 volts, followed by five minutes more at 600 ampères and 80 volts. About fifty reductions were made by this method. The reaction was occasionally vigorous, but never explosive, although 350 grams of powdered aluminum were used in some cases. The metallic oxides used were those of iron, nickel, cobalt, chromium, manganese, molybdenum, titanium and tungsten. The amount of retarder was diminished in the case of the less readily reducible oxides. In a few cases reaction could have been brought about by the usual method of an igniter, but owing to the presence of silica, boric anhydride, or both, most of the charges required the heat supplied by the electric arc to complete the reaction.

Having once established that the electric arc may safely be used to start and to carry to completion reactions in which finely divided aluminum is used, the application of the method is obvious. The heat of the electric furnace may be substituted for that formerly obtained by the addition to the charge of some easily reducible oxide, thus yielding pure metals instead of only alloys of titanium, tungsten, etc. A condensed account of such a combination of electric heating with the alumino-thermic method as applied by W. Huppertz to the production of titanium from rutile may be found in *Electrochemical Industry,* 1905, Vol. III, 35.

Laboratory of Applied Electrochemistry,

DISCUSSION.

Dr. Richards: This method of reducing oxides by means of aluminium as a strong reducing agent was first tried by Tissier; and the first time he tried it he blew his furnaces to pieces and very nearly lost his life.

The easily-reducible oxides are reduced with the evolution of such a large amount of energy that the local temperature is extremely high. The temperature probably reaches between 3000° and 4000° C., when an easily reducible oxide is reduced by aluminium. With iron, it reaches in the neighborhood of 2500° to 2700° C.

The more difficultly reducible oxides—those which, when reduced by aluminium, give a less excess of heat—are difficult to operate upon because there is not enough excess of heat in the formation of the alumina to melt the resulting alumina and reduced metal, and the reaction tends to stop itself.

The device which is used by Mr. Watts is that of furnishing sensible heat in the material which is to react, and therefore putting the reduction of these strong oxides on the same basis as the automatic reduction of the more-easily reducible ones. The mixture being heated up to bright redness, you have the amount of sensible heat which is in the mixture added to the excess of heat which is in the formation of alumina over that of the oxide reduced, and the resulting temperature is sufficient to melt the

oxide formed and the metal. A necessary condition for the reduction of these oxides is that the oxide formed, which is largely alumina, shall be melted as well as the metal.

In speaking of Mr. Rossi's experiments, there is a factor which has not been sufficiently taken into account. When the metal is reduced by aluminium the bath first of all contains a lot of the aluminium itself, and as the bath contains less and less of the aluminium to react, the energy with which it reacts upon the metallic oxide becomes less and less, being diminished by the energy with which the aluminium is alloyed with the metal; and, therefore, we have the difficulty of getting a pure product of these metals. The affinity with which the last of the aluminium is held in the alloy, puts a limit to the purity of the metal which can be obtained by Mr. Rossi's method.

President Bancroft: When working with an aluminum and iron oxide mixture on a small scale—for instance, in the lecture room—we have had great difficulty in getting really satisfactory results; and we have only obtained them by adding magnesium. I have been told that Goldschmidt also adds magnesium and that some of his chromium, when analyzed, contains traces of magnesium. I should like to ask whether any body knows anything about that as a fact. I merely state it as a rumor.

Mr. Burgess: It is true that you can start the reaction very much more readily that way; but if you want to go to a little more trouble you can eliminate the magnesium by using an iron fuse wire to start the reaction.

Dr. Richards: Perhaps your remark is caused by the fact that a little magnesium is used as an igniter or fuse. I do not think that any magnesium is put into the mixture, as an essential constituent. A little magnesium ribbon stuck into the charge is often used in the laboratory process and perhaps on a large scale used as a fuse for starting the reaction.

President Bancroft: In working with a small crucible, radiation is, of course, very high. We started the mixture with barium peroxide, but did not get satisfactory results without the addition of metallic magnesium. Of course, that would not mean that you would not get very good results if you were working with five kilogramme lots and a correspondingly lower radiation.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 19, 1905, President Bancroft in the Chair.

NEW GIN PROCESS FOR THE ELECTRICAL MANUFACTURE OF STEEL.

By Gustave Gin.

The new electric furnace which I have devised for the electrical manufacture of steel allows of the simultaneous and uninterrupted realization of the following operations:

Fusion, oxidation of impurities, reduction of dissolved oxide of iron, recarburization or introduction of the constituent elements of the final steel.

The accompanying design represents, to call it an example, one form of construction of a furnace accomplishing the conditions indicated.

Fig. 1 is the plan of the furnace.

Figs. 2 and 3 are transverse sections.

The furnace comprises essentially:

1. A crucible for fusion and refining by oxidation (1).
2. A compartment for reduction and recarburization (2).
3. A chamber for the observation of the color.

The electrodes of compartment (1) are connected to one of the terminals from the source of electricity, and the electrodes of compartments (2) and (3) are connected in parallel with the other terminal.

The current passes from the electrodes to the metal through a sheet of slag, which is the principal seat of the heating action of the current.

The baths of metal communicate by the openings (B) of sufficiently reduced section, in order that by reason of the Joule effect the metal may not remain solid.

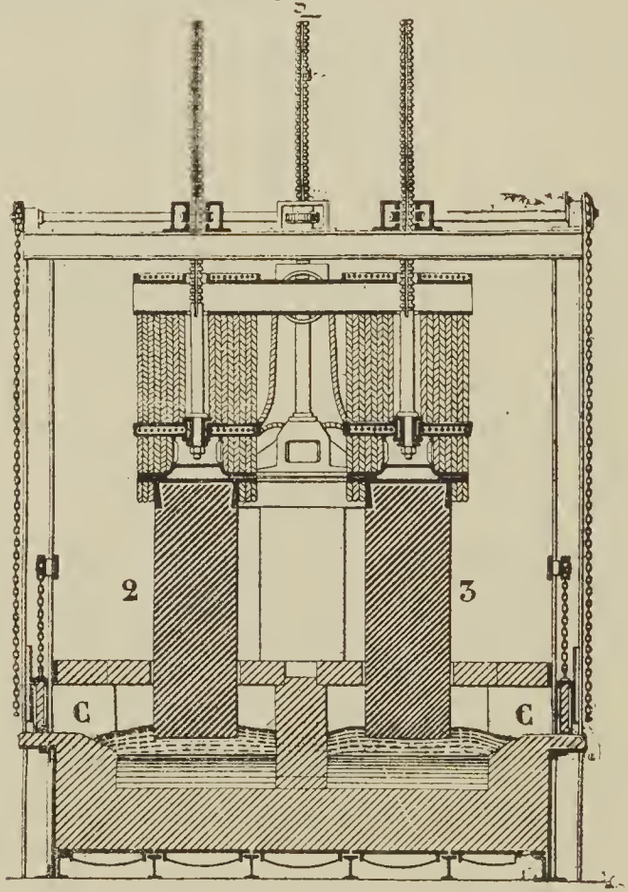
The fitting of the compartments is appropriate to their function: The base and sides of the oxidation compartment (1) are, in the part permanently occupied by the metal, constructed of a material basic or acid, according as the metal to be refined is or

is not phosphatic; but the part in contact with the slag should be neutral, of chromite of iron, for example.

In compartments (2) and (3) magnesia is employed preferably for the floor and surfaces not touched by the slag, and chromite of iron is made use of for the upper part.

To put the furnace into operation, melted iron or liquid steel is introduced through the orifice (A). It distributes itself through the three compartments on the floors of which scrap iron is strewn, the pieces being placed in connection with (B). Then arcs are created and little by little the material is introduced, which, after

Fig. 1



fusion, forms the superficial baths in which the Joule effect is produced.

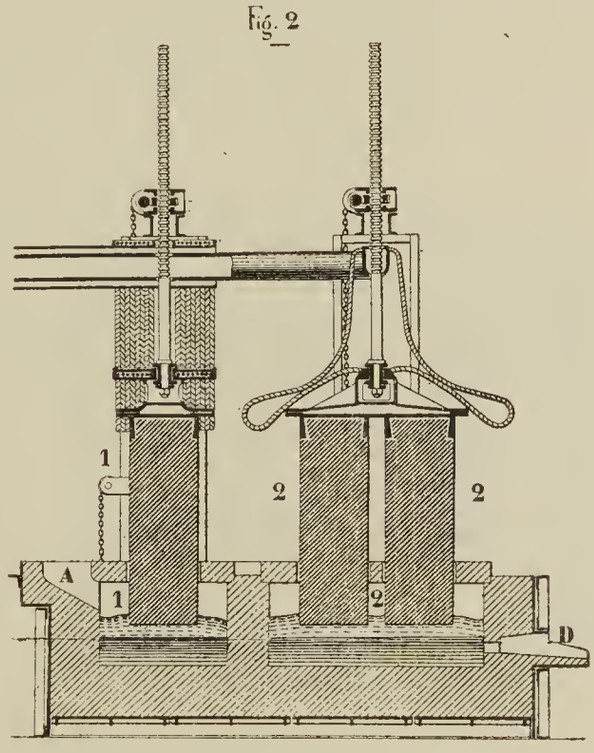
The oxidizing bath of compartment (1) is composed of some mineral or slag rich in oxide of iron, in addition some lime if the metal to be refined is phosphatic. The baths of compartments (2) and (3) are neutral and little reducible by carbon.

Aluminates of lime and magnesia, made from a mixture of bauxite, with limestone or dolomite, give favorable results. The addition of calcium fluoride makes it more fusible and mobile.

The functions of the furnace are characterized as follows: In the oxidation chamber the zone of most intense heat is, of course, found close to the contact of the metal and slag, and it is in this region that the reduction of the oxides is effected at the expense of the silicon, and of the manganese and carbon of the metallic bath.

According to the proportion of reducible oxides, the reaction is more or less rapid, and is evidenced by the turbulence of the bath, which stirs the metal and aids the oxidation by constantly changing the surface of contact. The oxidizing action is kept

Fig. 2



going and its intensity and rapidity regulated by the careful introduction of oxide of iron or by stirring.

Because of the high temperature, the elimination of the carbon is effected almost at the same time as that of the silicon and manganese.

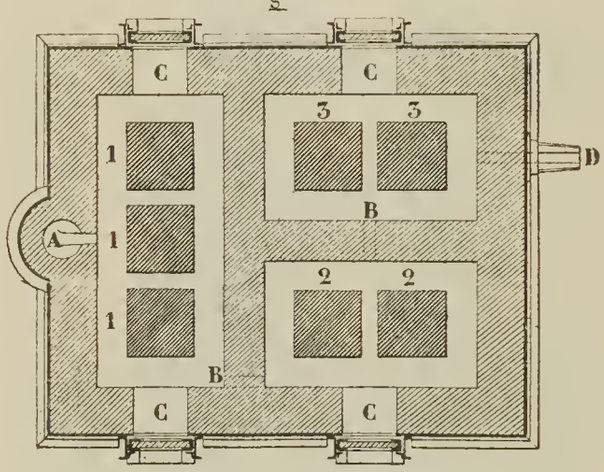
By means of the method of circulation adopted, the refined metal in (1) passes next into compartment (2), where the reduction of the dissolved ferric oxide and the recarburization of the metal takes place. Thus two operations are accomplished entirely by the admission of carbon in the form of coke, of iron or of casting specially prepared by the fusion of iron or steel in the electric furnace in the presence of a great excess of carbon. In raising

the metal to a sufficient temperature, a cast iron is obtained which absorbs as high as 77 per cent. of carbon, which it retains on cooling, partly as combined carbon and partly as intermingled graphite. It may be advantageous to introduce this carburetted cast iron in the liquid state, as when it comes out of the electric furnace.

The regulation of the recarburization or the incorporation demanded by the nature of finished steel, is accomplished in compartment (3), where some test ports are placed which allow one to estimate the color obtained and indicate additions to be made in correcting for impurities observed.

The necessary use in the Martin furnace of ferro-manganese or ferro-silicon to prevent the oxidation of the metal before the

Fig. 3



purification would be almost useless here. In fact, in the two last compartments the steel escapes all oxidizing action, for it has no contact whatever with the atmosphere, and only comes in contact with a neutral slag. Besides, this slag under the influence of the high temperature and the presence of carbon furnishes a slight quantity of aluminum, which diffuses into the bath of steel and absorbs oxygen in whatever form it might be present.

The charging of the solid material and the withdrawal of the slag is effected by means of the openings (C) and the stream of steel by the orifice (D) placed at a given height above the floor.

To tap the metal, the electrodes (3) are lowered and immersed in the metallic bath, at the same time that the electrodes (1) are raised, in order to maintain the voltage of the system. During

the pouring, the immersion of the electrodes (3) is increased in such way that the level of the metal remains constantly at the height of the pouring orifice. After the electrodes touch the bottom of the crucible, as the level of the metal can no longer be maintained, the latter falls until the slag appears in the flowing jet, which is then stopped.

The operation which has just been explained is of considerable importance. In fact the immersion of the electrodes prevents unequal levels between the compartments (2) and (3). There can be no mixing of the metals at the different stages of the refining, and metal can only be run off when refined thoroughly and to a known color.

The duration of the pouring being nearly constant, the dissolution of carbon through the immersion of the electrodes varies little, and it is possible to keep careful account and guarantee for the final product a determined color within narrow limits.

After tapping, electrodes (3) are raised again and electrodes (1) are immersed in the metal; part of the metallic oxide passes from (1) into (2), while the carbureted steel in (2) penetrates into (3). Thus the levels remain at their normal height, the electrodes immersed in (1) occupying simply the place of the steel which has just been left. If at this moment we tap the crude iron or incompletely refined steel in the first compartment, raising simultaneously electrodes (1), the metal introduced fills the space given by removal of the electrodes, but without ability to penetrate directly into compartment (2), for there is no sensible difference of level. The operations remain there distinct and independent and can succeed each other in continued rotation as long as the material retains sensibly the temperature of reduction, the capacity of the compartments being such that each tapping only represents a fraction of the metal present, the part remaining playing the part of a heat retainer.

Finally, it can be remarked that the metal in (1) passes to (2) without carrying the slightest trace of slag, which excludes all outside impurities.

DISCUSSION.

Mr. S. S. Sadtler: I might ask Dr. Richards whether he understands that paper as referring to a system of canals between these compartments. I was a little in doubt. In the author's original furnace the system was that of incandescent streams of metal heated by the Joule heat, and in his second paper (that reserved for to-morrow) there is an experiment described in which the electrical resistivity of the iron is measured in a canal of this kind; and I was wondering whether this system of worm effect was incorporated in the connection between these compartments 1, 2 and 3.

Dr. Richards: My understanding of it is that the furnace may be started by taking scrap iron; putting it in all the three compartments, placing bars of it through those orifices between the compartments and heating it up by direct contact with the electrodes, so as to get direct heat, then running in the fused metal so as to cover up the orifices and producing a slag. Afterwards the electrodes are shown only as dipping into the slag, the idea being that the current then passes from slag to metal in one compartment, through the ports to the other compartment and then out of the metal through the slag to the other electrodes. Undoubtedly this would cause great intensity of heating locally, at the ports, and keep the metal very fluid therein.

President Bancroft: As I understand the article, I should say that the improvement in the Gin process consisted chiefly in eliminating most of the characteristic features of the original Gin process.

Mr. C. J. Russell: I notice in the lower part of the first page it states that the current passes from the electrodes through the sheet of slag to the metal in the first operation, and later it is stated that the baths communicate by the openings "B", of properly designed section that by reason of the Joule heat the metal shall remain fluid. I rather think this is the answer to the question put by Mr. Sadtler—that while the entire bath is not reduced to the extremely attenuated channels which were originally contemplated in the Gin furnance, in these communicating passages the section is such that the Joule heat is just sufficient to keep the temperatures up to the proper point.

Mr. William Smith: I would like to ask Prof. Richards one question; and that is, if the carbon in the testing chamber is too low (which we all know does continually occur in practice in our open-hearth furnances) what provision they have for raising that carbon? Perhaps Dr. Richards can give us some information on that.

Mr. Sadtler: There are ports in all of these chambers where any thing can be introduced from the outside.

Mr. Smith: Those appear to be more like test holes for the introduction of reacting substances.

Dr. Richards: I think there is no doubt that the orifices "C," which are intended for removing slag, would be quite large enough for the introduction of any alloy which was needed. There is, however, very little provision made—or none at all—for the reducing of the carbon in the chamber "3". There would be no difficulty in *introducing* carbon by adding pig iron, or ferromanganese, or spiegeleisen, in order to bring it up; but if it were desired to reduce it, there would be difficulty, since it would have to be done by means of some metallic oxides such as the oxide of iron, and then the de-oxidation of the bath and bringing of it up to test would have to be done over again.

The idea of running the furnace is that the steel as it goes into chamber "2" shall be practically decarburized and then only enough carbon added to it in the form of spiegeleisen or ferromaganese to bring it up to just the desired point. There would always be the difficulty of absorption of carbon from the electrodes, if they were not kept immersed in the slag. Practically, I think that the weak point of the process is the means of separating the refined steel from the partly-refined and from the crude metal. If provision were to be made in some manner for closing those orifices from above, so that the steel could be removed from compartment "3" easily without there being any connection between it and compartment "2": then I think it would be practically possible to run out a properly refined steel. But if there is continuously connection between that and the compartment "2" and compartment "1", I hardly see that it would be possible to tap out the steel without its being mixed with the partly refined metal.

Mr. Sadtler: I think Prof. Richards' question is answered

in the next to the last paragraph on page 109, in which it is shown they can raise the electrodes in one compartment, or lower them, just as they need to, to raise or lower the level of the steel or slag.

President Bancroft: In the second paragraph on page 108 it is stated that the recarburization is carried out by means of those test ports. Does not that cover the point raised?

Mr. Smith: The test ports are usually very small—just enough to run a small test out into a testing mold—and would scarcely be large enough, except in very small quantities to insert the Pig iron or whatever alloy you want to use to raise your carbon; and I do not think where the chambers are joined together at the bottom and the metal can flow from one to the other; that it is possible to stop the impurities from going from one chamber to the other.

In the handling of steel in tests made to run iron and steel together in a mold (which has been done a number of times), the carbon in the steel side will be absorbed by the iron, even with a thick steel plate between the two; so that if the carbon will pass through a steel plate, even where there is no communication between the two layers of molten metal I think it is a very difficult matter, where there is an opening to allow the metal to pass from one chamber to the other: to prevent those impurities from passing with the fluid metal and do not think it can be done in practice.

Mr. Barry MacNutt: I would like to know how the electrodes are connected electrically. It states on the bottom of page 108 that "at the same time that electrode '1' is raised in order to maintain the voltage of the system"—does that mean that the electrodes are in series?

Dr. Richards: I have read over the paper very carefully, to try and find statements as to the circuit. On page 105 it says that the electrodes of compartment "1" are connected to one of the terminals from the source of electricity and the electrodes of compartments "2" and "3" are connected in parallel with the other terminals. It does not say whether they are used as anode or cathode, nor whether alternating or direct current; but the circuit is evidently from compartment "1" to the other poles in compartments "2" and "3."

MR. MACNUTT: The ports "B," then, form electrical connection for the current.

DR. RICHARDS: Yes.

PRESIDENT BANCROFT: Unless otherwise stated to the contrary I should assume that he was using alternating current. That is usually employed in these electrical furnaces.

DR. RICHARDS: My remembrance is that the Héroult furnace or the Héroult patents were based on the dipping of the electrodes only into the slag and not into the metal; and in that respect the furnace would possibly come into conflict with the Héroult idea.

MR. C. J. RUSSELL: I would like to ask as to the impression of the members present on the general efficiency of this furnace from the layout shown in this paper. It would appear from the section that the radiating surfaces of the electrodes and containing chambers are very large compared with the metal baths. That would make it appear inefficient in operation and require an excess of energy. That is only my impression. I would like to hear more on this subject from those present who have had experience with furnaces.

DR. BANCROFT: At the St. Louis meeting last summer M. Héroult stated that M. Gin was not yet making steel commercially.

MR. SMITH: I would like to ask (for I am in the dark and am seeking for information, and that is the reason I am up here) whether there is any gentleman present that knows of any furnace in the United States that is making steel commercially at the present time. If there is, I would like to get in communication with that gentleman as I am very anxious to follow up this line of melting steel.

DR. ROEBER: There are now quite a number of experimental steel furnaces of different types in operation in this country. The first case of the applicaton of the electric furnace for steel making on a commercial scale in this country will be at Syracuse at the Holcomb Steel Co. Works, where an 80-ton electric steel furnace of the Héroult type will be started in October or November.

DR. BANCROFT: I will ask Dr. Waldo to tell us any thing that he feels like saying in regard to this paper, or in regard to the electrical manufacture of steel by this or any other process.

Dr. Leonard Waldo: Mr. President, and Gentlemen of the Society: I feel honored to be asked to speak to this distinguished body and I am pleased to be asked to speak on this subject; because the metallurgy of steel has received a new baptism in the presence of our enormous sources of power and the certain use in the near future of electricity in engineering units in the melting of steel, and those of us interested should unite in disseminating the results of our experience.

Papers of the kind read are somewhat unfortunate, in that they do not conform to the rules of papers that govern papers presented to the Institution of Civil Engineers of England. It does not describe results accomplished, but describes proposed methods. Now those of us who have been somewhat familiar with the handling of electrical currents where the heat function has been highly developed, know the extreme difficulties of handling enormous currents where the voltage is low and the amperage is high. It is a question of the survival of the fittest; it is a question of the consumption of your electrodes, if they are made of carbon; and it is a destruction of the containing cylinders and pots if it is a question of the vehicle in which the molten steel or molten iron is contained.

Quite a number of years ago, when I was connected with the Cowles' Lockport Works and at the beginning of the industry, we were impressed with the construction of the 200 kilowatt generator, which was then called—not the "Colossus of Rhodes" but the "Colossus of Niagara." The other day I turned to my friend, Dr. Wheeler, as we were looking at some work, and I said: "What are those?" And he said: "Those are the castings for the 7,000 kilowatt machines that are to go to California; and there are eight of them in the works" so the time has come when the electrical energy can be furnished by the state of the electrical arts in sufficient amounts to seriously consider it in metallurgy.

In all of the old metallurgy it has been necessary to deliver current through an electrode, in which case the management of the electrode becomes extremely difficult. At some time or other the current through the electrode either passes through a mixed charge with varying resistance, or makes an imperfect contact. When that happens, the current arcs; and when it arcs, you have

the practically uncontrollable temperature of 3850° C. and you have a corresponding impurity and a corresponding difficulty and a corresponding intense action of the single point of the arcing.

I have had occasion to design furnaces in which the Siemens type had development; but after use I made up my mind that the best way was to have no arcs, and to have no current anywhere except in the metal which you are melting. Unfortunately at the time of first conceiving of the induction furnace the problem of the alternating dynamo had not been developed; and the problem of the alternating current transformer was in a still less satisfactory shape.

A few years ago a gentleman in Sweden owned a paper-mill. This paper-mill was not over profitable and finally burned down. In order to utilize his water-power it occurred to him to see what he could do in making Swedish steel. From that sprung the Kjellin process, which at this stage was promptly successful because dynamos and transformers could be built; the theory was understood.

Without reverting in any detailed way to the development of the same problem in the United States, let me point out what that problem becomes. Suppose that we have a square transformer, Obviously you can put on one leg of the transformer a ring-shaped crucible, and on the other the ordinary primary coil, and then if a sufficiently powerful alternating current is sent through the primary, your secondary becomes heated and its voltage is decreased as its single turn is less than the turns of the primary and your amperage is proportionally increased, assuming for the moment that resistance losses are negligible. We have there the ideal condition in metallurgy; because you have the containing crucible with no electrodes, no contact with fuel in any shape; the efficiency becomes enormously high under a properly constructed transformer; the current furnished is outside of your whole melting cycle; and the melting takes place at any rate you wish.

This control of the rate of heating is a most important advantage. We all know how long it takes after a crucible reaches a white heat before the final complete fusion takes place. The induction furnace permits us to add quickly the energy units

which makes final minutes in the melt take the place of almost hours when the high temperature is making costly radiation and racking the mechanical stability of crucibles and furnace construction alike. At high temperatures approaching the melting point, it is possible to push the rate of temperature increased to 1°C per minute by adding 2 kilowatts for every 100 lbs. of steel or to put it practically you would raise your steel the last 200° C. by adding 4 kilowatts for 10 minutes.

In my judgment for most metallurgists—at least in operation on a moderate scale—this is the coming type of furnace, for reasons given. If a furnace chamber is built of the proper material its life in indefinite. The heat is generated wholly within this chamber and not in excess of the fusion requirement.

I am afraid, gentlemen, I have not strictly discussed Mr. Gin's paper; but I should very much like to ask the Chairman whether this furnace had been operated.

President Bancroft: The Chairman is absolutely non-committal on any such subject.

Dr. Waldo: The efficiency of the induction type of furnace is extremely high, the best furnaces melting a ton of steel with an energy consumption of 500 K. W. hours. Of course, in this type of furnace the coal efficiency rises very much over the coal efficiency in the crucible form. In the crucible forms I take it that most of us have been quite well satisfied there is an efficiency of 2.8 or 3 % of the heat units in the steel melt of those which go into the furnace in the shape of fuel. Of course, in this case you burn your coal or use your water-power, which is a better solution of the problem under the most favorable conditions, with the very best boilers; and you operate your furnace with compound engines of the highest efficiency and you realize at that stage of the operation all the gain which you have in the highest types of boilers and engines combined. For in the rest of the cycle the loss is extremely small.

Unfortunately, the mathematical electricians have very largely neglected the theory of transformers when very large currents are developed in the Secondary and, with the exception of some fragmentary statements by Kapp in the last German edition of his "Transformers," the subject is almost wholly undealt with and does not find itself in the scientific papers or transactions of tech-

nical societies; so that much of the ground that has been gone over is entirely new in that respect; but with a properly designed furnace and transformer the entire loss in the rest of the cycle, from the engine and furnace on, hardly exceeds 15% and may be less than that. I hope, gentlemen, I have not wearied you; but I really felt, in bringing up this subject of electrical furnaces before a society of your standing, that something ought to be said to render it less fragmentary than the paper which was read and left with comparatively small discussion. Thank you very much.

THE PRESIDENT: The society is very much indebted, indeed, to Dr. Waldo for what he has told us of his induction furnace. It practically constitutes another paper and puts the whole subject on a much more satisfactory basis. I think I also voice the sentiments of the society in expressing the hope that at some future meeting Dr. Waldo may see fit to give us a paper on the same subject such as would meet the standard of the Institute of Civil Engineers, both qualitatively and in actual results. This being practically a new paper, I think it is quite likely that some of the audience may feel inclined to discuss it as it stands.

MR. HERING: The furnace which Dr. Waldo described is an extremely interesting one, but it has been known for a great many years during which it was not used; and it would be interesting therefore to hear from Dr. Waldo what the nature of the improvements are, which have made it a success, if it is really a success now. I would like to ask, also, whether this induction furnace is now being operated on a commercial scale, other than the application by Kjellin.

DR. WALDO: In reply to Mr. Hering's very pertinent questions, the state of the art has had much to do with its present efficiency. At the time to which Mr. Hering refers—the time of Ferranti and his succesors—neither the alternating current dynamo nor the transformer could be built of the efficiency with which it is to-day. Mr. Edward A. Colby built the first of the American furnaces and almost contemporaneously the engineering firm of Sprague, Duncan & Hutchinson independently experimented with one of their own construction.

Concerning the operation of the furnace in a commercial way, I would refer Mr. Hering to the elaborate papers by Engelhardt in January, February and March 1905 numbers of "Stahl und

Eisen," where the furnace has been discussed and where analyses are given and products of steel made with the Kjellin furnace process (which is essential in its ideas with some of the other forms) are described.

DISCUSSION.

(Communicated after adjournment.)

Mr. Gustave Gin: It is very gratifying to me to ascertain the interest taken in the subject of electric steel by the American Electrochemical Society, and I am glad to be a member of an organization the scientific development of which is marked by such earnest concentration.

In the discussion following my communication I notice some uncertainties which I wish to clear up.

One member has asked if the migration of impurities through the connecting passages was not possible between the compartments and into the refined steel. I have noticed in my furnace at the works at the Plettenburg Canal, that the diffusion currents in the steel under treatment are evidenced almost exclusively in the form of vertical eddies, the effects of which are very slightly felt in the horizontal direction, with the result that one can obtain steels of entirely different composition at points but slightly separated in the same passage. Nevertheless this objection has a certain value as to carbon, which is diffused very rapidly, and to assure a perfect result I have thought to provide a vertical compartment in the duct in which I simply introduce an ingot of steel. This ingot, while it does not exactly fill the section of the passage, suffices to prevent the mixture of the baths as long as there is no difference of levels. Again this ingot naturally offers no measurable resistance to the passage of the current. It melts little by little and settles automatically in the chamber which holds it in place. You will find the details of this expedient in the plan of my oscillating furnace in the report which I am sending you.

Another remark was made which concerns a possible conflict between my furnace and that of Héroult. It is easy to reply to

this by stating that I took out French patent No. 263783 on Feb. 6, 1897, for the manufacture of steel in a furnace utilizing the Joule heat in the slag. I have, therefore, nothing to fear on the grounds of priority of invention.

There remain the comments of Dr. Waldo, who after unimportant opening remarks, has expressed regret that there should be presented to your Society reports concerning furnaces which are not in commercial operation. Then he has spoken at length of the Kjellin furnace, reiterating without exact facts, things that are well known and commonplace.

Every person has a right to his own opinion, but I also have the right to protest against the insinuation which would present me in the light of an office electrometallurgist only. I hold the record of the world for the construction of electrometallurgical works, and as for steel, I have not only built the small works at Plettenburg but am now starting the construction of the works at Oberhasli, the capacity of which will exceed 60,000 H. P.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 19, 1905, President Bancroft in the Chair.

AN ELECTROLYTIC PROCESS FOR REFINING SILVER.

By Anson G. Betts.

There are in practical use two electrolytic refining processes, known as Moebius Process and Balbach, after the inventors, which differ in the means adopted to prevent the spongy silver deposits from reaching the anodes and short-circuiting the cells. Certain objections to these processes appear, among which are the ungainly apparatus used, high resistance of the solution, collection of the silver in a loose condition with consequent trouble and the necessity of inclosing the bullion anodes in cloth bags to keep the gold out of the electrolytic silver. There are also certain chemical objections in the requirement of anodes practically free from other metals than copper and silver and the more precious metals. Lead in the anodes is said to go into lead peroxide, especially when the solution contains copper, and this lead peroxide is hard to get out of the gold residue. A process that would work well with lead and other metals in the anodes in considerable amount would be quite an improvement, as cupellation and refining of the bullion before electrolytic refining, with attendant costs and serious losses, could be done without.

Present progress in the recovery of silver is in the direction of collecting the silver of the ores ultimately as an anode slime from the electrolytic refining of base metals. This anode slime will contain the bismuth of the ore, and this is at present mostly wasted, the amount thus lost apparently being considerably greater than the total present consumption of the metal.

From researches conducted in lead depositing the conclusion was reached that the best results would be obtained with salts of strong acids forming soluble silver salts, nitric acid being excluded, of course, on account of its oxidizing nature. Accordingly solutions were made up with dithionic acid as silver salt and free acid.

Dithionic acid is a strong acid, and forms a very soluble silver salt. It is practically equivalent to sulphuric acid, and could be replaced by sulphate of silver in such an experiment but for the fact that sulphate of silver is not sufficiently soluble.

An experiment was conducted as follows by Dr. E. F. Kern:

No.	Solution.	Contents in 100 cc.	Current Density per sq. ft.	Time.
1	$AgNO_3.HNO_3$	4.3 gr. Ag. 1 gr. HNO_3	2.2	50 hr.
2	$AgKC_2N_2.KCN$	4.3 gr. Ag, tr. KCN	2.2	50 hr.
3	$Ag_2S_2O_6.H_2S_2O_6$	4.3 gr. Ag, 1.5 gr. $H_2S_2O_6$	2.2	50 hr.

	Grams Silver Deposited	Remarks.
1	17.917	Inferior spongy deposit.
2	18.292	Very good, solid deposit.
2	18.626	Fairly dense and smooth, but not solid

Dr. Kern then made an experiment with the dithionate solution with organic and inorganic reducing agents.

Cell No.	Added.	Remarks.
1	1/120 000 gelatine	Fairly good.
2	1/120,000 gum arabic	Best, fairly solid.
3	1/60,000 tannin	Fairly good.
4	1/60,000 hydrochinon	Spongy.
5	1/12,000 formaldehyde	Spongy.
6	1/12,000 acetone	Spongy.
7	1/12,000 aniline	Spongy.
8	1/2,500 SO_2	Fairly good.
9	1/2,500 benzol	Spongy.
10	1/2,500 toluol	Spongy.
11	1/2,500 CS_2	Spongy.

A number of similar experiments were then conducted along these lines, using in addition glucose, dextrose, resorcin, and benzoic acid, but it was found that gum arabic and dextrose gave rather the best results. Many of the solutions became turbid from reduced silver. It was not found possible to get with regularity a really first-rate deposit from this solution, although it gave decidedly better results than the nitrate.

Experiments were then made with methyl sulphuric acid, prepared by the reaction at about 100°C., with an excess of concentrated sulphuric acid on methyl alcohol (one part methyl alcohol

and seven parts strong sulphuric acid heated several hours at 100° gave a yield of 82.5 per cent. on the methyl alcohol), pouring the mixture into water or ice, and adding litharge, white lead, chalk or barium carbonate until the free sulphuric acid is precipitated. To make the silver solution, the acid is partly neutralized with litharge, and silver sulphate added, precipitating lead sulphate and leaving silver methyl sulphate in solution.

After similar experiments with this solution it was found that one part of gelatine or gum arabic added to twelve thousand parts of the solution influenced the deposit favorably, but not very considerably. Larger additions caused a dark-colored sediment to separate from the solution and often gave a black cathode deposit. This solution gives a very good deposit without any such additions. Carbon disulphide was not tried at first because it had not given good results with the dithionate solution, but it has since been found to be the best addition, as too much does not do any harm by causing black precipitates.

The deposits obtained were hard and solid, free from "treeing," but lack tenacity. This, however is not an objection of weight in silver refining.

Lead, copper and bismuth in the anodes go into solution along with the silver, leaving gold, selenium and tellurium as a residue. Bismuth methyl sulphate shows no tendency in strongly acid solutions to separate into a basic insoluble salt, which is a great advantage. With solutions containing 15 per cent. free acid, bismuth may rise to 4 per cent. without decomposition of the salt.

The next step is to reconvert the lead, bismuth and copper methyl sulphates back into silver methyl sulphate. There are a great many possible ways of doing this effectively, but the plan adopted consists in first precipitating silver still left in the solution with metallic copper, and then throwing out the copper and bismuth as metals by precipitation with metallic lead. The next step consists in treating the solution with silver sulphate, made by dissolving silver in hot concentrated sulphuric acid, producing insoluble lead sulphate and solution of silver methyl sulphate. This method is, however, open to the objection that the precipitated lead sulphate carried with it considerable silver, so that it appears that there is room for an improvement here, for example, by precipitating all lead from the solution with sulphuric acid, and

then dissolving silver carbonate (made by digesting silver sulphate with soda) in the solution. It should be mentioned that silver sulphate is obtainable as a by-product from boiling the gold slime with concentrated sulphuric acid to get the silver out of it.

The mixed precipitate of copper and bismuth can be well treated with ferric sulphate, thus extracting the copper in solution and leaving the bismuth as oxide.

Troy, N. Y.

DISCUSSION.

PRESIDENT BANCROFT: I should like to call attention to the fact that in this precipitation of silver Mr. Betts states that gelatine and gum arabic act equally well; whereas we were told yesterday that gum arabic would not do at all—that gelatine was the only substance that had this peculiar property.

MR. BETTS: Gum arabic is not of any general use in depositing other metals. It happens to be in this case; but it does not in general,— you cannot depend on a colloid to make a metal solid unless it will always do it; and you also have other substances which are not colloids, having the same action. We have carbon bisulphide in solution in this case, which is the best of all. Also sulphur dioxide, a non-colloid, has some effect.

PRESIDENT BANCROFT: The carbon bisulphide, according to Gore's analysis is decomposed and some sulphur comes down with the silver.

MR. BETTS: Yes, and that hardens the silver. I think that accounts for the tenacity of the metal.

MR. S. S. SADTLER: I should like to ask about this methyl sulphuric acid and methyl sulphates, do you not find them expensive to prepare?

MR. BETTS: They are formed by the interaction of concentrated sulphuric acid and methyl alcohol, at about 100° C.; it takes some eight to ten hours to complete the reaction. I would also like to say something about the stability of this acid. It breaks down into methyl alcohol and sulphuric acid in the presence of water; but I found it would take years to complete the reaction, or even to carry it to a large extent, at ordinary temperatures.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 19, 1905, President Bancroft in the Chair.

ELECTROLYTIC VS. SULPHURIC ACID PARTING OF BULLION.

By F. D. Easterbrooks.

The essential elements of a parting process are: production of silver free from gold at a low cost, equal to the strictest commercial requirements, and operating with great neatness. These conditions are more easily attained with electrolytic than with sulphuric acid parting, although at the present time the larger portion of the bullion produced by the lead and copper refineries is parted by the latter method. Electrolytic parting processes have not as yet been generally adopted.

The purpose of this paper is to point out some of the principal characteristics of the several parting methods.

With the sulphuric acid method refined gold can be produced, ready for shipment, twenty-four to thirty hours after placing the bullion in the kettles, which is several days earlier than is possible with an electrolytic method. This is advantageous in those cases where the Doré is high grade and interest charges have to be considered. A daily cut-off of the gold treated can be made, and thus a quick check obtained of output on input. There is also almost no silver tied up in plant, as in the electrolyte and cathodes of an electrolytic process.

The acid solution from the reducing tank containing the copper used to reduce the silver sulphate solution is disposed of in either of two ways: the bluestone crystallized on lead strips and the mother liquor concentrated and used again in the kettles, or, as is the case in copper refineries, added directly to the electrolyte, in which case the value of the acid added per ounce of silver parted, after deducting the power cost of depositing the copper in insoluble anode tanks, determines the amount at which an electrolytic parting process must operate below the sulphuric in order not to exceed the costs of the latter, since with an electrolytic parting process sulphuric acid must be bought especially for the copper electrolyte.

There is a loss of acid at the kettles while dissolving silver in sulphuric acid. This loss depends partly upon the rate at which the process is conducted and on the efficiency of the condensing apparatus, but in any case amounts to a considerable percentage of the amount used.

Another objection to the acid method is the non-elimination of tellurium from the silver during parting. This element materially affects the physical properties of the silver with which it is alloyed, small quantities causing it to crack at the edges while being rolled. In Fig. 1 is shown the effect of alloying, in varying

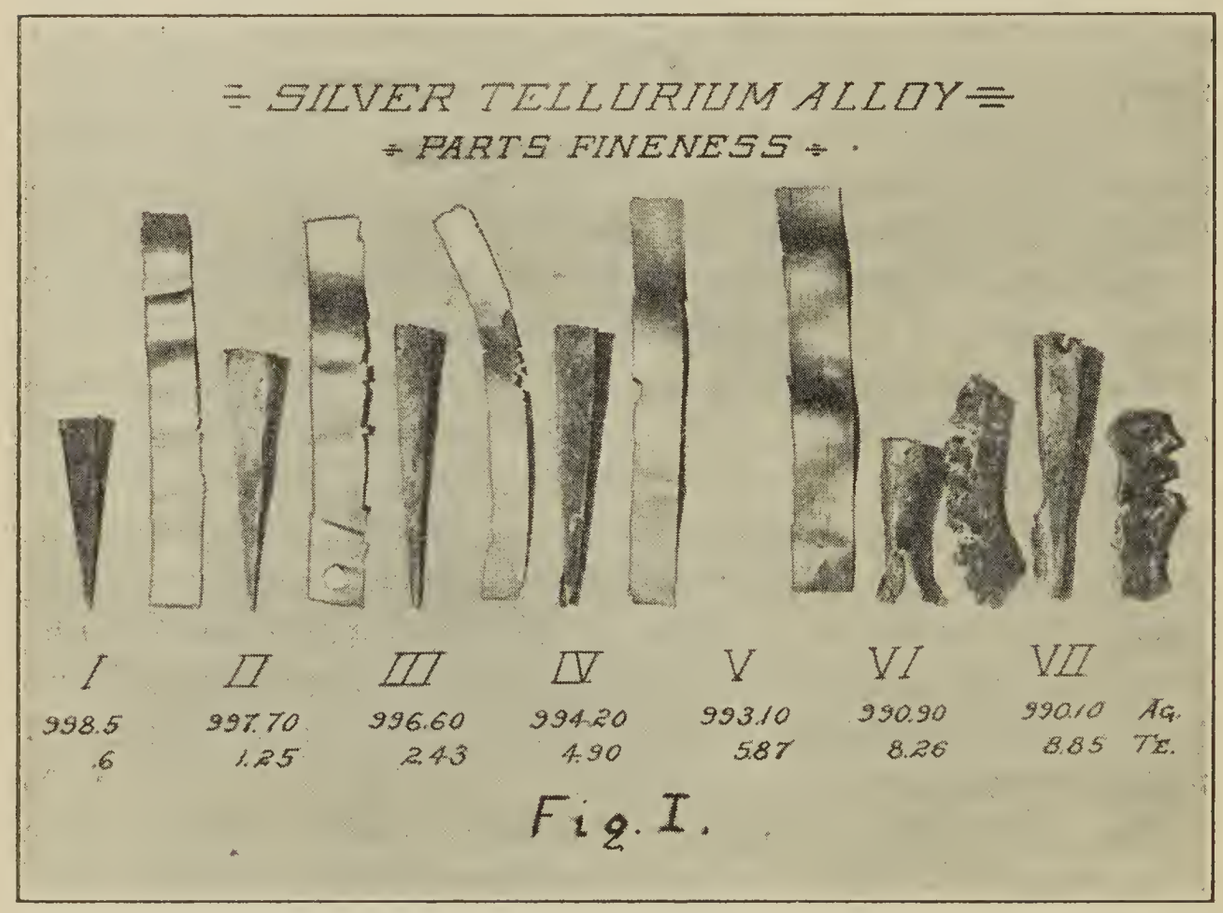


Fig. I.

amounts, tellurium with fine silver. The pointed pieces were hammered hot, the strips rolled cold. In the hammered piece of sample No. 3 is seen the first crack due to tellurium. Fig. 2 gives an enlarged view of this sample.

In minting operations the fine silver is first alloyed with 10 per cent. copper. One-part per thousand of tellurium in the silver will cause this alloy to crack when rolled out. Five-tenths to six-tenths part per thousand (.05 to .06 per cent.) is the probable safe maximum amount of tellurium that silver can contain

and meet minting requirements. To produce silver from material containing much tellurium, so that the refined product will not contain more than the above maximum allowable amount, requires, when parting with sulphuric acid, an exposure of the bullion in the Cupel to air and nitre for a considerable length of time. This is shown by the following illustration.

The usual quantity of slimes were melted in a Cupel furnace. After skimming the slags, two Tuyere pipes two inches in diameter

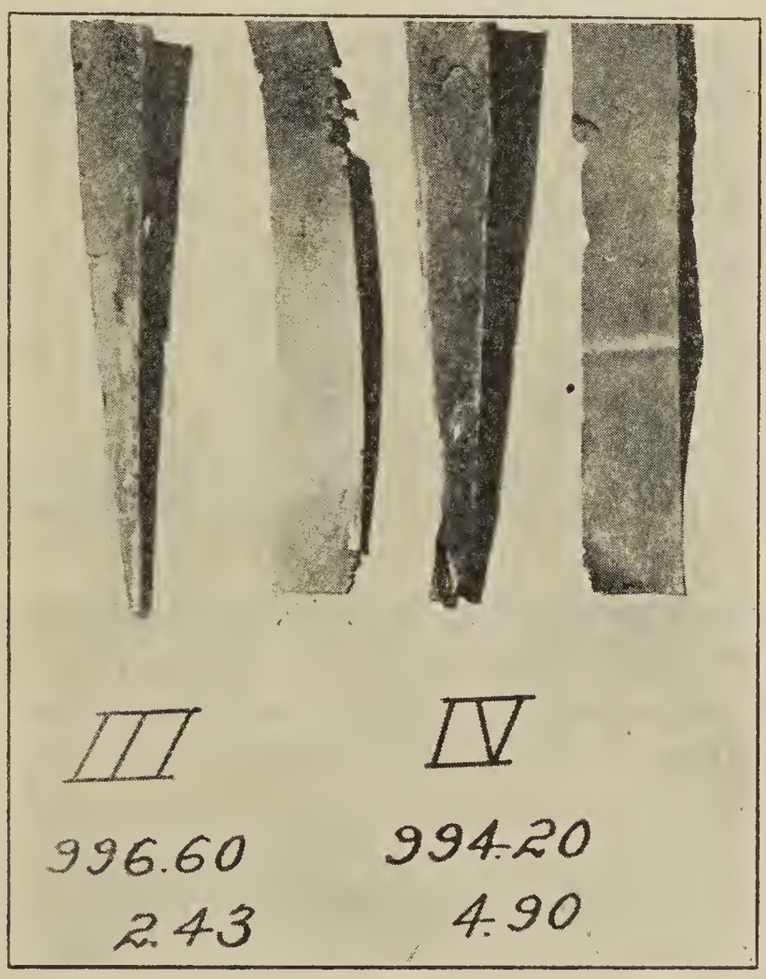


Fig. 2

were placed so that air under five ounces pressure blew directly on the surface of the bullion. Nitre was used freely. Twelve and one-half hours were required to eliminate sufficient tellurium to secure a refined product of the requisite fineness. The analysis of the several samples are given in Table I, which shows also the early removal of the selenium.

This bullion represented by sample E was parted with sulphuric acid, and the refined silver contained .6 part of tellurium.

TABLE I.

Elimination of Tellurium and Selenium. Charge No. 59.

TIME TAKEN.	PARTS FINENESS.			
	Te.	Se.	Ag.	Au.
Sample A—April 8, 5.00 A.M.	34 30	13.45	903.72	15.98
" B " 9.00 A.M.	23.40	.81	939.47	16.53
" C " 1.00 P.M.	5.36		968.61	17.19
" D " 3.00 P.M.	2.41		973.35	17.25
" E " 5.30 P.M.	1.31		973.46	17.04

A portion of the same lot parted electrolytically contained not a trace.

With electrolytic parting we have a choice of two distinct systems of depositing silver on the cathode, one in a loose crystalline form at a relatively high current density, as in the Balbach and Moebius methods, the other with the aid of gelatine in an adherent form at a lower current density.

The electrolyte used is a copper-silver nitrate solution, although recently Betts[1] has proposed using a silver methyl-sulphate solution.

These methods all have in common the characteristic of producing fine silver free from gold and tellurium at one operation, the deposited silver being melted and poured into bars without any further refining, as in the sulphuric acid process. Silver placed in the tanks as anodes is not handled until taken out as refined silver, whereas in the acid method the silver either in solution or as cement must be transferred several times with the aid of siphons, steam, etc., before it is in a condition to be melted. For these reasons it is possible to operate an electrolytic parting plant with a higher degree of neatness and cleanliness (such as the value of the material treated requires) than is possible with acid parting.

A parting plant using the Balbach method is simple in construction and operation. Fig. 3 shows the cross-section of a tank. The cathode is made of one-half inch Acheson graphite slabs fitted to the bottom. Two silver contact pieces rest respectively on the bullion to be parted and the graphite slabs. Bullion cast in thin square slabs is contained in a cloth case which is supported on

[1] Electrochem. Industry, April, 1905.

a wooden frame suspended over the tank. The gold slimes accumulate on the under side of the bullion, between it and the cathode, increasing the resistance as the operation continues. Each tank has a cathode surface of eight square feet and a current density of 20 to 25 ampères per square foot is used. The voltage averages 3.8 per tank, and an average ampère efficiency of 93 per cent. was obtained on a continued run, while occasionally an efficiency of .98 per cent. was secured. The power required is 31.5 watt-hours per ounce of fine silver produced.

Most of the silver is deposited on the cathode surface directly under the anode, and the reduction of the distance between anode and cathode is limited by the space necessary to reach in and remove it, which has to be done frequently on account of the silver

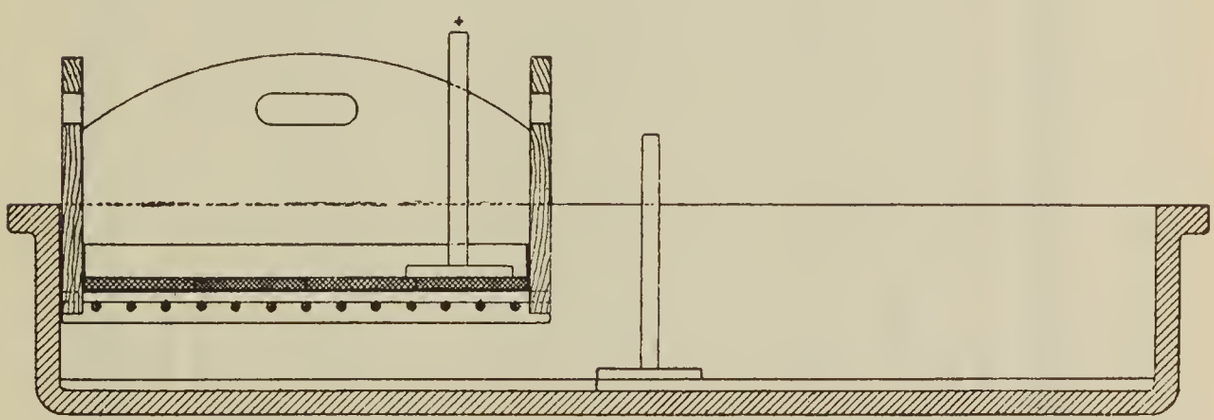


FIG. 3

Cross Section Balbach Tank.

bridging across to the cathode. This serves also to agitate the electrolyte. There is gassing in this tank and the consumption of nitric acid is much higher than in the Moebius method.

At 20 ampères per square foot about 32 per cent. of the daily output of each tank is held permanently in stock in electrolyte and contacts, which is less than is retained in the Moebius method.

In Fig. 4 is shown the cross-section of a Moebius tank. They are arranged in units of six placed end to end, each unit being provided with apparatus for raising the boxes containing the deposited silver together with the anodes and cathodes, and with arrangements for imparting a reciprocating motion to the wooden scrapers. There is no system of circulating the electrolyte, but the scrapers moving back and forth agitate it. The

anodes are contained in a cloth frame which holds the gold slimes, and the silver is brushed off from the silver cathodes by the wooden scrapers, and drops into a box with hinged bottom. It is removed by raising the boxes above the top of the tanks and emptying it into a tray placed beneath. This operation requires one-half hour per day per unit. Each tank has a cathode surface of about 16.5 square feet, and a current density of 20 to 25

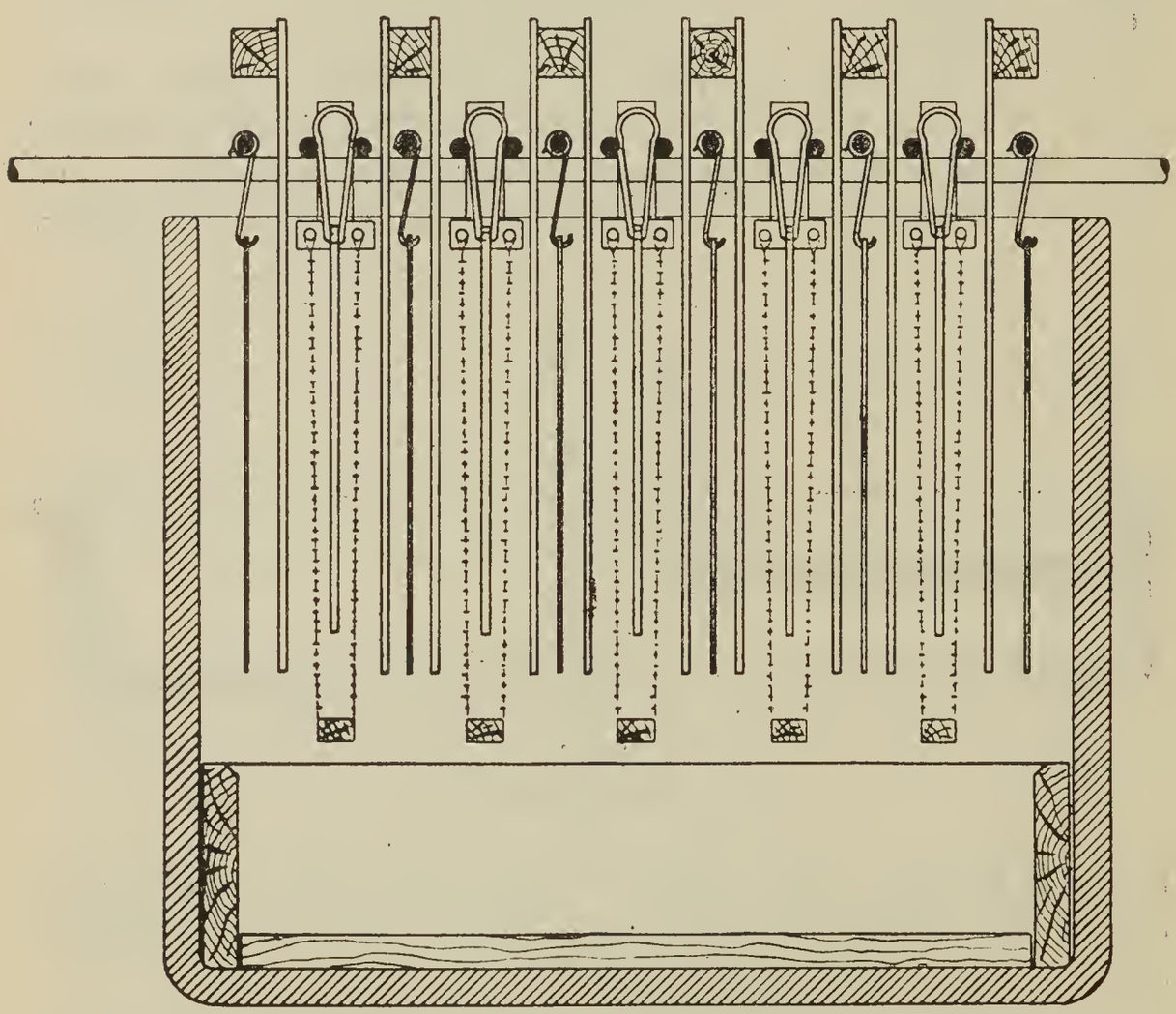


FIG. 4

Cross Section Moebius Tank.

ampères per square foot is used. The voltage between electrodes is 1.4 to 1.5, and the power cost is 13.2 watt-hours per ounce of silver deposited. An average ampère efficiency of 94 per cent. is obtained. At 20 ampères per square foot 41 per cent. of the daily output of each unit is permanently held in stock in cathodes and electrolyte.

The necessity of cutting out of service the units of a plant using

the Moebius method to remove the silver, and the frequent siphoning off and replacing of portions of the electrolyte in each tank in both the Balbach and Moebius methods, to maintain it of fixed compositions, are objections overcome by depositing the silver on the cathode in an adherent form.

This method permits of an arrangement of tanks and electrodes and a system of circulation of electrolyte similar to that used in the multiple system of copper refining.

The finely divided condition of the gold in the bullion, which in commercial work rarely contains more than 40 parts per thousand, requires that the anodes be inclosed in a cloth frame to keep the deposited silver free from gold, as the light, fine particles do not fall to the bottom of the tank with sufficient rapidity. A current density of 10 ampères per square foot is used, and the power cost is nearly identical with the Moebius method. 28 to 32 per cent. of the daily output is retained in cathodes and electrolyte.

Gold from either the sulphuric or electrolytic parting process can easily be produced of a fineness of .990 or above, free from silver. The Government charges for melting and assaying such gold is so low, varying from .6 to .9 cents per ounce, depending on the weight of the bar, that there seems to be no immediate possibility of an electrolytic gold-refining process, such as the Wohlwill, becoming an attractive commercial proposition, except in those cases where platinum is present and the output large. Such a process would increase costs by delaying shipments, with loss of interest on gold in process, and that permanently held in stock in cathodes and electrolyte, and by increasing labor costs with no increase in the value received for the gold.

DISCUSSION.

Mr. A. G. Betts: I would like to ask Mr. Easterbrooks if he ever gets dark deposits of silver in this solution of nitric acid when he has gelatine in it. I have tried that and found you get a cloudy formation of silver through the solution; then the deposit often turns black or blue. It seems to me very interesting to think that he has got such a beautiful deposit as that shown in that way.

Mr. Easterbrooks: A good deposit is obtained by adding a small quantity of gelatine daily, using a low current density and maintaining a rapid circulation of the electrolyte.

Mr. S. S. Sadtler: Do I understand you do not recommend either the Moebius or the Balbach?

Mr. Easterbrooks: While both the Balbach and Moebius processes are good methods for parting bullion, a process which will deposit the silver on the cathode in a more or less solid form would be an improvement, in that it would permit of a simpler or more convenient arrangement of plant.

President Bancroft: Why is the voltage so high in these other processes? We have silver electrodes and yet there is a voltage of 1½ volts as against 0.3 volt in the copper refining? Of course, the current density is low in the copper refining, but not low enough to account for that difference.

Where does the counter-electromotive force come from when you use silver electrodes? Is it from the formation of silver peroxide?

Mr. Easterbrook: Taking the Balbach cell where the voltage is 3.8 as an illustration, the electrodes are further apart than in a copper cell and the copper-silver electrolyte containing 5% free HNO_3 has a resistance of about 3.3 ohms per cubic inch, which is several times greater than a copper electrolyte, at the temperatures in general use in the respective methods. The counter electro-motive force which, in this cell amounts to .15 V is also greater than in a copper cell.

Dr. J. W. Richards: I think one cause of the higher counter-electromotive force (if you wish to call it that) is the fact that the solutions are not as conducting as are used in the copper refining. With the electrodes I have seen used, as close together as in copper refining, you cannot operate with any thing like the same voltage, because of the lack of conductivity of the electrolyte, which cannot be made strongly acid, but must be worked nearly neutral.

Mr. Easterbrooks: The amount of acid is very low, usually about .12 in plants using the Moebius method.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 19, 1905, President Bancroft in the Chair.

INSULATING PAINTS.

By Maximilian Toch.

Electric traction is responsible for a new industry. With its invention came new types of electrical appliances, and the methods and materials used on steam roads were supplanted by different equipments.

A steel bridge over which a new trolley line passes soon shows the effects of the decomposition of the steel, and this deterioration we call electrolysis. A road which is run by the third-rail system soon shows evidence of oxidation in spots hitherto unnoticed. Against these ravages insulating paints, compounds and varnishes are used, and while many of these materials are excellent when they are first applied, they become useless in proportion to the conditions to which they are subjected. This subject is really so vast that it is only possible for me to touch on the topic in a general way, and I shall endeavor to bring out that materials which are designed for a tunnel are useless in the sunshine. The materials used in tunnel work must withstand moisture, and unless they do that they will disintegrate, until eventually they form conductors. As a rule, the black paints for tunnel or underground work are composed of bitumens. The bitumens as a class are of the polymethylene group, and their structure is one atom of carbon and two of hydrogen combined many times, and moisture will neither add to nor subtract from this structure. On the other hand we have the fatty acid oils which form the bases of many good insulating paints, and when they are used in damp places they are not split up, but added to, and their value as an insulating paint is lessened.

A study of the bitumens shows us that sunlight destroys them, and the two atoms of hydrogen combine with oxygen to form water and carbon is set free. Consequently, we notice that a bitumen insulating varnish soon becomes smutty, due to the

liberation of carbon, and we are therefore justified in the deduction that for exposed use bitumen is not to be relied on, excepting where it can be replaced every few months.

If we take sugar and add to it strong sulphuric acid, a reaction takes place which demonstrates to us that sugar is composed of carbon and water, and inasmuch as sulphuric acid has a great affinity for water, the reaction is complete. Without going into a lengthy detail of prolix organic chemistry, I might say for the purpose of demonstration that many of the bitumens and waxes are acted on by acid in this manner, and as we have 14 per cent. hot acid solutions to deal with in the electrolytic deposition of copper, it is most interesting to observe the action of the acid on the various insulators, and those that appear best in the beginning are ofttimes the soonest to fail.

The time of drying is often a factor in the life of the insulating paint. The slow-drying paints should never be subjected to aqueous liquids until drying is complete.

Cross Arm Paint.—A very high resistance is not so essential as one that will withstand the elements, and a liquid medium which soaks into the pores of the wood is better than one which dries by oxidation and forms a film which peels.

Third-rail Paint.—A third-rail is subjected to oxidation and so violently, too, that it is often found necessary to replace it sooner than the running rail. The sides or web of the rail can be protected with a paint which will resist corrosion and short circuiting. The top is sometimes covered with a wooden guard. This guard must be painted with a fire-resisting and insulating material.

Return Wire Paint.—It is remarkable how corrosion takes place along a return wire, and the metal surrounding these places is usually coated with oil paint containing lead and zinc. It has taken practical demonstrations to convince some mechanical engineers that such paints produce or superinduce electrolytic corrosion, and strict vigilance and copious applications of the correct materials are necessary in such places.

I would, therefore, earnestly recommend to professors of electro-chemistry to take up this subject with their students, and allow them to work out for themselves subjects of this kind. There is no reason why a third-rail paint should not be made,

one that will stand both dampness and sunshine for a year. There is also no reason why insulating materials should not serve as a protector to metals against oxidation as well as electric currents. Fortunately, we have records of the preservative action of many paints on wood and metal, and it only remains now for us to work out the proper combinations, and to this end chemists who have a technical training ought to be employed by colleges to give students occasional lectures on raw materials so that they obtain a fundamental training in the theory of coatings. A student who knows these things has a better future in store for him and an easier chance for employment.

DISCUSSION.

Mr. Carl Hering: In the author's abstract of this interesting paper, he made one statement in it which is so contradictory to what many consider one of the fundamental laws of electrolysis, that I think attention should be drawn to it. The statement is, that in one experiment there was electrochemical oxidation on the cathode. One of the fundamental laws of electrolysis, as I understand them, is that the current invariably produces a *reducing* action at the *cathode* and an *oxidizing* action (in its broad sense) at the *anode*. Perhaps the discrepancy is due to an error in assuming which electrode was the cathode.

Mr. S. S. Sadtler: As far as I can see, that is a case of chemical action rather than electrical, the formation of the water by the combination of hydrogen and oxygen, will form a wet film absolutely in contact with the metal, and always inside of the surface oxidation. At the anode, on the other hand, there would be no such film formed. This film of water would be a better medium for absorbing carbon dioxide and other chemical agents which produce rust. It is not so much the oxygen that produces the rust, but the formation of a bicarbonate of iron in a reduced state, which is at once oxidized by the air with the elimination of CO_2.

President Bancroft: That has already been studied in one case. If you make iron the cathode in an ammonium nitrate solution, the iron does dissolve; and of course if it dissolved, it

could then very easily be reprecipitated by air as ferric hydroxide. I do not know whether this is analogous to the case under discussion, but it meets Mr. Hering's objection.

MR. HERING: In dissolving it, does it not, perhaps, reduce something else? In other words, is there not really a reducing action there?

PRESIDENT BANCROFT: I think not. There is formed in the electrolyte a substance which reacts with iron. The reaction of the iron can be considered as an entirely independent, secondary chemical reaction; but all the same it does take place and you have the electric current producing the substance which reacts with the iron.

PROF. W. S. FRANKLIN: It may be due to the formation of an alloy of ammonium and iron which goes into solution like the sodium lead alloy.

MR. HERING: Zinc may be dissolved (oxidized) on a cathode; but that is a secondary reaction and is subsequent to the primary electrochemical one. It is not due to the electrochemical action of the original case.

PRESIDENT BANCROFT: As I understand it, the fact that interested Mr Toch was that the iron plate which was the cathode at times did rust. I do not imagine that he cares whether the actions are simultaneous or whether one follows the other.

PROF. C. F. BURGESS: I am glad this subject has been brought up; because I have made some observations which make me believe that a metal serving as a cathode may under certain conditions corrode more rapidly than when no current is flowing, and I hope to hear a further discussion of this point.

Statements are occasionally made by practical men that the current flowing toward a water-pipe will cause it to oxidize more rapidly than if no current is flowing. This is somewhat contrary to the commonly accepted views of electrolysis. It is also assumed by some that the alternating current will promote rust. Some of my students have made extensive laboratory tests on both these matters and found we can get conditions whereby both the alternating current and the current flowing toward the cathode will cause corrosion to take place more rapidly than when under ordinary conditions. A very striking experiment of this sort may be performed by taking an iron plate; putting it in a

rather strong sulphuric acid solution and running the electric current toward that plate. The plate will corrode more rapidly than under ordinary chemical conditions. Now whether this is a chemical action pure and simple or whether it is partially electrical action, the electrical current has the effect of increasing the oxidation of the cathode—"oxidation" being used here in its broadest sense. Just whether it is a physical action of the current or some chemical action I am not prepared to say. In some cases the current flowing toward the cathode will protect it from the chemical action of the solution; in other cases it will greatly facilitate the corrosion.

Prof. William B. Schober: I understood Mr Toch to say originally that hydrocarbons—particularly those of the methylene or polymethlyene series in the form of bitumens or other similar compounds—form an effective insulating agent in the dark. Is that statement true?

Mr. Toch: Yes, that is correct.

Prof. Schober: When you are dealing with saturated or unsaturated, fatty acids, do you find that you get the same insulating effect in the dark, or that they are better insulators in the light?

Mr. Toch: The saturated or unsaturated fatty acids act fairly well in the dark, provided they are not subjected to moisture; because these groups of acids will be saponified with water The moment, of course, you have a hydrolyzing action with fatty acid of that kind, you lose whatever dielectric you had in the beginning.

President Bancroft: If you saturate an iron plate with hydrogen and then expose it to the air, it seems to me quite conceivable that we might have a simultaneous oxidation of the hydrogen and the iron by some sort of autoxidation process. We have some experts here on autoxidation. Could we get any information from them on this particular problem? Apparently not.

Dr. J. W. Richards: I am not an expert on autoxidation; but the simultaneous liberation of hydrogen in contact with the iron may very probably form a couple in which the iron may suffer from oxidation with reference to the hydrogen; but when hydrogen is oxidized in the presence of an oxidizing agent water is

formed; and it is to me quite conceivable that the presence of the water formed aids in the oxidation of the iron—that the continual production of water thus formed from the oxidation of hydrogen is a determining factor in increasing the rate of oxidation of the iron.

I would like to say that, if any of the members wish to see Mr. Toch's paints, the electrochemical room at the other end of the laboratory is painted with asphalt paint of that make, and we find it extremely satisfactory in our electrochemical work as being both acid-proof and heat-proof.

PRESIDENT BANCROFT: It seems as though there were several ways in which a cathode might corrode, and that we do not know very definitely, as yet, what the special method is in this particular case.

MR. SADTLER: There is always more or less leakage of the current to the steel work of elevated structures, etc. When surfaces and the soil are damp, there would be a considerable leakage current flowing, with the evolution of hydrogen at the cathode surfaces and more or less alloying with the metal and the formation of a finely divided iron such as is the case with the lead we have just discussed. Then the water dries up, the leakage current is turned off and then the chemical action of the moisture and the carbon dioxide of the air sets in.

MR. TOCH: I cannot help but agree with Mr. Sadtler on that point; for on a bridge which shows electrolysis you get a tremendous amount of oxidation, and visible oxidation. For instance, it is not generally known (I hope to make it so, though) that the ordinary rust, as we have all been brought up to believe, was a yellowish body which is a hydrated oxide of iron. As far as I know I have isolated two other kinds of rust and determined their formulæ also, and the kind of rust that is formed by electrolytic action is not the rust that you would recognize with the eye for a moment; it is a brownish rust which has a totally different formula, being a mixture of $Fe_2O_3 + 2H_2O$ and $Fe_3O_4.H_2O$.

PRESIDENT BANCROFT: Is it not possible that this brown oxide you mention may be one of the brown oxides described by Haber and Kaufmann in their paper on the electrolysis of ammonium nitrate solutions with iron electrodes?

MR. TOCH: How long ago was that written?

PRESIDENT BANCROFT: It is in Volume VII of the *Zeitschrift für Elektrochemie.* It was four or five years ago.

MR. SADTLER: In giving references authors refer to the numbers of volumes of the different journals; and as there are so many published, in many different countries, it does not convey the information as to time of appearance to the average reader. In our Transactions I think we ought to have a regular rule of converting volume numbers into dates—say 1901 or 1902; then everybody knows just how far back to look. In editing the Transactions we must have some uniform system; and I have generally been using the Italic designation of the volume; but I think it would be very much better if we used dates hereafter.

PRESIDENT BANCROFT: A still better suggestion, it seems to me, would be to put in both the volume and the date, because in looking up references you usually want the volume. It is an advantage to have the date in. In my own references I always put in both volume and year. I am sorry to say that in a great many cases people do not put in the year.

MR. HERING: An oxidation at the cathode by the original current is so contrary to modern ideas of electrochemistry, that it seems to me that in any case in which this appears to occur, the action needs further investigation.

PRESIDENT BANCROFT: I quite agree with Mr. Hering, but I might offer the further suggestion that it depends entirely on how modern one's ideas are.

MR. A. B. LARCHAR: An experience of mine may shed some light upon the matter of oxidation of a cathode. We had an electrolytic cell where we were electrolyzing brine. The anode was graphite. The cathode was steel, and the entire apparatus was enclosed in a steel tank which formed part of the electrical circuit. Now it occurred that when the contact between the cathode and the steel tank was sufficiently imperfect to necessitate a voltage of more than 1½ to cause the current to pass from cathode to tank, the alkaline solution on the outside of the cathode would decompose and the cathode was ruined. In other words, the cathode became the anode of another system (cathode, alkaline solution and tank), and it may not be impossible that the plate there (indicating sketch on board) which is marked the

cathode, became the anode of some other electrolytic system under conditions prevailing in Mr. Toch's experiment.

Mr. Hering: This will probably be found to be the correct explanation in many other cases in which there appears to be oxidation at the cathode.

President Bancroft: I think not necessarily, because I understand that in the Castner process for making caustic soda they have to be very careful indeed, what sort of iron they use for the cathode, otherwise it is acted on by the caustic soda. That, of course, can be considered purely as a chemical reaction of the cathode electrolyte; but the cathode does corrode, and when you come back to it that is really the important point. Since the solution which causes the cathode to corrode is produced electrolytically, it seems to me that one is justified in speaking of that as an electrochemical corrosion of the cathode.

Mr. Hering: But not necessarily due to the action of current.

Mr. Larchar: Under ordinary conditions, i. e., with good contact between cathode and tank, there was no corrosion; and while you may run the density of the caustic soda up to where it contains 200 grammes to the litre, there is absolutely no action on the cathode.

President Bancroft: Will it do so if you use a cast iron cathode?

Mr. Larchar: I am familiar only with the steel cathode.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 19, 1905, President Bancroft in the Chair.

THE UTILIZATION OF ACTIVE OXYGEN ELECTRICALLY AND CHEMICALLY PRODUCED.

By Richard von Foregger, Ph.D.

There must be some reasons why, lately, the chemistry of oxygen in its various forms has conspicuously attracted the attention of the scientists as well as of manufacturing chemists. It is, of course, always the unproven that stimulates investigation, and there is no doubt that there is a great deal of unknown and unproven in the physiological as well as the technical chemistry of oxidation.

Inasmuch as the theories of autoxidation are becoming better understood new fields are open for practical developments. But our theoretical knowledge in that branch of chemistry is far ahead of practical experience. A number of chemical processes are said to be based upon an indirect oxidation, which our practical knowledge would scarcely have recognized as such. The full recognition of the facts, however, might cause a pronounced change and a considerable simplification in a number of processes of applied chemistry.

When we are told by research men that the chemical reaction of benzoic acid in food preservation or of formaldehyde in purification is based upon a secondary autoxidation, we would hardly believe it, yet a study of such theoretical assertions will lead us to important conclusions and the facts will no doubt prove again what a great field is still awaiting the utilization of electrically and chemically produced oxygen in *statu nascendi.*

We have two kinds of autoxidizers which are direct sources of active oxygen; one is ozone, the other is represented by certain peroxides, chiefly of the alkaline and alkaline earth metals. Both are based upon the same principle of formation, which may be expressed as follows:

$$A_n + (O_2)_m = A_n(O_2)_m$$

whereby n and m be any even number.

In their decomposition, *i. e.*, their formation of active oxygen, there is a similar likeness.

Ozone is split up in $O_2 + O<$

A dioxide is split up in $AO + O<$

According to Nernst the formation and dissociation of ozone is illustrated by the following equilibrium:

$$O_3 \rightleftharpoons O_2 + O$$

$$O_2 \rightleftharpoons O + O$$

In assuming, according to the latest theories, that among the three atoms of ozone only one atom enters into activity, the other two forming molecular or inactive oxygen, we have an even basis on which to compare the action of ozone and of our peroxides. The molecule O_2 in ozone takes the place of the lower oxide of a peroxide, both being acceptors or carriers of available oxygen. In a peroxide the amount of available O varies according to the degree in which the superoxidation took place. In calcium peroxide, for instance, we have as highest yet obtained 72 per cent. dioxide, which represents about 16 per cent. available oxygen. To my knowledge, comparative tests as to the efficiency of action of nascent oxygen of ozone and nascent oxygen of a peroxide have never been made. We have, however, the right to assume that both are the same, as the vehemence with which the unsaturated affinity of an atom O hastens to combine is always the same in the same medium.

These two sources of active oxygen—ozone and certain peroxides—compared from a practical side, show the one as a gas and the other—with the exception of hydrogen peroxide—as a powder. The first has to be produced at the place of consumption, in practical use by electrical energy in its various forms. It is an unstable gas which cannot for practical purposes be stored and has to be utilized immediately after its formation.

The second of our sources, peroxides, are stable, transportable, storable and automatically entering into reaction whenever required with a fixed or determinable amount of energy. This shows that peroxides are transportable accumulators of available oxygen, a fact which at once renders evident their superiority in many respects to ozone. The advantages indeed are such as to open to the chemistry of oxidation new fields, which heretofore

could not be exploited by ozone and partly also not by the liquid peroxide, hydrogen peroxide.

Let us first review in which fields active oxygen and molecular oxygen have been employed so far, and in which possible fields they may become valuable factors.

That oxygen is a vital part of life is beyond dispute; beginning with the rôle it plays in animal and plant respiration and ending, as to our knowledge, with its gift to feed the cells of organized tissue. While organic life has been described as a slow process of oxidation, or of combustion without flame, we find at the same time that oxygen is the condition of all combustion and that it is of value wherever an effect of light or heat is to be obtained. Besides this, oxygen accomplishes in nature three main features which, in proper reproduction, will become indispensable factors in industrial work. Oxygen disinfects, it purifies and it bleaches. It is a strikingly interesting fact that the same element which creates and supports life also safeguards and defends life, in destroying microbes and immunizing decaying substances which are the enemies or the negative part of sound life. In the full recognition of this feature lies the greater part of the future of the chemistry of oxygen.

According to the above outline we have, then, the following schedule of the various fields in which oxygen is a factor of utility:

First. Oxygen as an element of evolution and oxidation in life.

Second. Oxygen as chemical energy for oxidation in the broadest sense, viz: effect of light, effect of heat, oxidation of inorganic substances.

Third. Oxygen as a disinfectant and purifier, or oxidation of organic matter.

Fourth. Oxygen as a bleaching agent.

The fields in which ozone as well as active oxygen derived from peroxides have been tried and are now partly utilized with more or less success, are:

The sterilization and purification of water.

The sterilization and preservation of food substances.

The purification of air.

The ageing of alcoholic beverages.

The purification of mineral oils.

The bleaching of vegetable oils.

The bleaching of textile fibre.

The bleaching of sugar and molasses.

The bleaching of corn.

The extraction and refining of gold. (Here, as well as in certain metallurgical processes, molecular oxygen is becoming extensively used.)

Finally, it remains to mention the use of active oxygen for medical purposes.

In these branches, besides ozone, sodium peroxide and hydrogen peroxide are being employed as direct sources of active oxygen. Owing to recent accomplishments several peroxides may now be added to the list. They are the peroxides of magnesium and calcium, which, on account of their non-toxic nature, may become of great value in the line of sterilization and the bleaching of edible oils, molasses, etc. There are, further, zinc and strontium peroxides and perborate, which may become of value in bleaching processes, certain metallurgical processes and in their medical application.

With these available data on hand we may now investigate what possible chances there are for an industrial use of these related forms of oxygen.

From an expert as well as from a human point of view the sterilization of water may interest most of us. The same is being accomplished by means of electrically operated ozonizing plants, but can also be accomplished through chemical means by the use of peroxides.

The first report on an industrial sterilization of water by means of ozone dates from the year 1891, and originated from Froehlich, engineer of Siemens & Halske. In consequence the German Government took the matter up. The first authentic figures which I have in hand come from Dr. E. van Ermengem, who demonstrated the ozonization of water before the Ministry of Agriculture in Belgium. Dr. Ermengem found that 5 litres of ozonized air, containing 15.2 mg. ozone per litre, destroyed 3,717,000 bacilli per c.c. of water within ten minutes; that is, 15 grms. ozone per m^3, which is a high figure compared to the results obtained in ozonizing plants which are now in practical use in several large European cities and in Philadelphia. There, from

1 to 9 grms. of ozone per m^3 water, it is stated, are sufficient to produce sterilization.

In their calculation Siemens & Halske take the basis of 2 grms. ozone per m^3 water, and they figure (*Ztschr. Electrochem.*, 1904, p. 13) the total cost in a plant of a capacity of 2,000 m^3 water per hour at 0.2 cents per m^3 water, and of a capacity of 200 m^3 water per hour at 0.7 cents per m^3 water. In proportion, the cost of a plant of a capacity of 20 m^3 water per hour would be 2.45 cents per m^3 water.

That would render the total cost per kg. of ozone, respectively, $1, $3.50 and $12.25; or, $3, $10.50 and $37.75 per kg. of active oxygen.

The United Water Improvement Co., of Philadelphia, operating the Vosmaer system, figure according to Arthur W. Ewell (*Electr. World and Eng.*, 1905, p. 267), on the use of 1 to 5 grms. of ozone per m^3 water, an output of 15 grms. of ozone per kw. hour, with an ozone density of 3 grms. per cubic meter. The cost of operating is from $3 to $9 per million gallons of water, or per kg. of ozone, 25 to 58.4 cents, or 75 cents to $1.75 per kg. of active oxygen—figures which are strikingly low when compared with those of Siemens & Halske, and as I do not know if they are approved by the Philadelphia concern, I think I can look upon them skeptically. The cost of the plant or an amortization is probably not taken into account.

Now let us see how the cost of active oxygen derived from calcium peroxide would compare with the cost of active oxygen derived from ozone.

Assuming that we have a 65 per cent. calcium peroxide, *i. e.*, a preparation containing 65 per cent. dioxide (CaO_2)—the rest being monoxide or oxyhydrate—corresponding to 15 per cent. of active oxygen, and assuming that the cost of 1 kg. calcium peroxide is $2, we find that 1 kg. contains 150 grms. available oxygen, and, therefore, the cost of 1 kg. active oxygen is $12.50.

Taking the figures of Siemens & Halske of 0.67 grms. active O per m^3 water as a basis, we find that the cost per m^3 water sterilized by means of calcium peroxide is 0.84 cents. Allowing the high addition of 20 per cent. for operating expenses and amortization of the little machinery that is required, we obtain a total cost of 1 cent per m^3 sterilized water. This would be

slightly above the figure of Siemens & Halske given for the total cost per m^3 in a plant of 200 m^3 capacity and is, of course, considerably higher than the figures attributed to the Vosmaer system in Philadelphia. But as the latter figures are not official and contain no explanation whatever, I think it is wise to neglect the same.

To be just, it must be said that this total cost occurring with calcium peroxide will not be reduced further than to a certain limit above 0.84 cents, even if the operation takes place on the largest scale, as in this event the calcium peroxide counts almost as exclusive expense. On the other hand, for the same reason, the total cost can hardly surpass 1 cent per m^3, even if the operation is done on a very small scale.

If this chemical method of ozonization compares, then, with respect to cost, slightly to a disadvantage with the electrical ozonization when used for large communities or in plants above 200 m^3 water per hour, it must be admitted that for smaller plants it offers an obvious advantage in cost. But there is another advantage which renders this process in every respect worthy of consideration, *i. e.*, its simplicity. There is practically no machinery required. A tank fitted with a stirring apparatus, and, eventually but not absolutely necessarily, a filter, and one man to handle it—that's all that is required.

The calcium peroxide is applied in powder form as it comes from the manufacturer, and an equivalent of sulphuric acid or an organic acid forming an insoluble calcium salt, as, for instance, citric acid, is added to hasten the liberation of active oxygen and to precipitate the calcium. The bactericidal action is complete in the time from five to thirty minutes, and the resultant water is just as pure and good as could be.

The reduction of time required for the peroxide process, compared to the time it takes to pass the necessary amount of ozonized air through the water, should also be noticed. Theoretically the yield of ozone in grammes per e. h. p. hour is 1.030. Practically, in the various systems an efficiency of 17½ per cent. seems to be the highest ever obtained, but the yield as usually found in working plants does not amount to more than 1 to 5 per cent. of the theory—the Siemens & Halske output, for instance, being 25 grms. and the Vosmaer output being only 11.2 grms. ozone per

e. h. p. hour. Therefore, if an increase of ozonization per m^3 water is to be obtained, an allowance of time and energy has to be made, as there is only a limited amount of ozone available per unit of time and unit of space. With peroxide, the increase of oxidation is obtained by an allowance of the density of action, which is simply produced by using more peroxide per unit of space. No allowance of time need to be made; on the contrary, the time of reaction can be shortened by an increase of peroxide. In other words, it takes one hour to pass the amount of ozonized air containing 0.65 grm. active oxygen through 1 m^3 water, and it takes one instant to charge 1 m^3 water with 0.65 grm. active oxygen derived from the peroxide.

The main value of this peroxide method consists, however, as mentioned above, in its use outside of the sterilization plant and without the aid of any apparatus. If I call calcium peroxide or magnesium peroxide transportable means for sterilization I mean to say that we are able to carry available oxygen around in our pockets ready for sterilization of our drinking water at any place.

Tablets of 0.1 gr. magnesium peroxide and citric acid which I made and submitted for trial to Dr. Park, director of the Board of Health, New York, were found to destroy within one minute 2,250,000 typhoid bacilli per c.c. in a drinking glass holding 150 c.c. water. The amount of 0.1 gr. magnesium peroxide or 0.08 gr. active oxygen per 150 c.c. water is, of course, unnecessarily high for practical use.

The Frenchman, Ed. Bonjean, in treating Seine water with calcium peroxide, obtained complete sterilization in using 0.02 gr. active oxygen in 1 pound water. If the same experiment was made on a large scale, hardly one-tenth of the amount of active oxygen would be required.

It would lead us too far to discuss the matter of sterilization and preservation of food by means of ozone or peroxides. Those interested I refer to the United States patents of Van der Brook for preservation by means of oxygen and ozone, and to the patents of Marchand for preservation by means of hydrogen peroxide. Both patents are of older date and, to my knowledge, are not in use. It is to be assumed that the powder form of the new peroxides is more apt for a rational utilization. I refer besides to an

editorial of the Boston *Medical and Surgical Journal,* March 9, 1905, entitled "Active Oxygen as Food Preservative."

As a second instance for the use of ozone and active oxygen I will mention that of bleaching. There are several electrical processes in existence to bleach textile fibre, oils, sugar and certain extracts. It seems, however, as if the excessive cost of these processes would not allow them to become of general commercial value. The success with which sodium peroxide has been introduced in this country as well as in Europe for bleaching textile fibre and straw vouches for its commercial adaptability.

Although the oil industry avails itself of very economical bleaching methods, it seems as if it would greatly welcome a practicable oxygen bleach, especially for the treatment of edible oils where the attachment of any foreign taste or flavor has to be avoided, and where food laws also prove restrictive to the use of substances which are not doubtless uninjurious to health. It appears, therefore, that here would be an open field for the application of ozone or of peroxides.

The ozonization would not only bleach the oil, but also absorb any rancid taste adherent to oils after treating the same and eliminate earthy taste due to the treatment with fuller's earth or silicate.

A. Levat treated olive oil in an apparatus for water electrolysis with low voltage and found that the bleaching of the oil started on the negative electrode and that the taste improved considerably.

Pummerer, in his process of bleaching linseed oils, keeps the oil in closed vessels at ordinary temperature, submitting the same to a current of ozone, using a pump which forces the gas through the oil as long as an absorption takes place. The oil thus treated is claimed to become decolorized, brilliant and siccative.

To my knowledge, no figures have ever been published proving the commercial value of these methods, and I do not know of any concern in the United States that is using one of them.

De la Coux, in his elaborate book, "L'Ozone et ses Application Industriels," in talking about bleaching of oils, says:

"In perborates we possess most energetic oxidizing agents, containing from 10 per cent. to 16 per cent. active oxygen."

This is true, and by the German manufacturers of perborate, the Deutsche Gold und Silber Scheide-Anstalt, Frankfurt-am-

Main, I am informed that a perborate process for bleaching olive, cotton and linseed oils is now becoming extensively used, and this with a cost of 0.16 cents per kg. oil.

In a series of experiments which I made with cottonseed oil, as a substitute for olive oil, I used calcium peroxide and found that ⅛ per cent. of this material furnished satisfactory results as to shade of bleach, and that in taste and flavor the oil was rather improved and by no means hurt. I figure that the cost of this process will be about ¼ cent per kg. of oil.

Now I will say one word about the value of oxygen in mining and metallurgy. Here oxygen is to a greater extent employed in its molecular form, its active state following under circumstances during the course of chemical reaction.

To most of you is probably known the controversy between McArthur, the inventor of the cyanide process for extracting gold, and Elmer. McArthur bases the reaction occurring in the cyanide process upon the following principle:

$$2Au + 4KCN + 2H_2O = 2KAu(CN)_2 + 2KOH + H_2.$$

He always claimed and still claims that the presence of oxygen during the process is of no value whatever. Elmer, McLaurin and Gogder, on the other hand, claim that the presence of oxygen is essential, and describe the reaction as follows:

$$4Au + 8KCN + 2H_2O + O_2 = 4KAu\,(CN)_2 + 4KOH.$$

Since publication of the results of investigations made by Bodlander *(Ztschr. f. angew. Chem., 1896,* p. 583), we can say that this question is settled. He proved that in the reaction the amount of oxygen which is put into activity is nearly the same as the amount of oxygen which combines (about 72 per cent.). With the theory of dissociation on hand he then came to the following process:

$$2Au + 4\overset{+}{K} + 4\overset{-}{CN} + 2\overset{-}{OH} + 2\overset{+}{H} + O_2 =$$
$$= 2Au\overset{-}{(CN)_2} + 4\overset{+}{K} + 2\overset{-}{OH} + H_2O_2.$$

Gold, during its solution in potassium cyanide, at the presence of air or oxygen is then a pseudoautoxidator, *i. e.,* it produces first the secondary autoxidator K or H, and K or H produce the autoxidation forming potassium peroxide hydrate or hydrogen

peroxide. The secondary process then of the solution of gold may be expressed as follows (See Engler & Weissberg: Autoxidation):

$$2Au + 4KCN + H_2O_2 = 2KOH + 2KAu(CN)_2.$$

The more peroxide formed—dependent on the presence of oxygen—the quicker the solution of gold. Gold-mining experts may have come to this result by practical experience, despite the contradictory assertions of McArthur. It is probably due to this fact that considerable quantities of sodium peroxide are being used by gold-extracting concerns. Of late, sodium perborate has attracted the attention of that part of mining experts, as borax, which besides peroxide of hydrogen is formed in the solution of perborate, seems to be a suitable medium.

A practical confirmation of the theory of the value of oxygen in the cyanide process is found in the so-called double treatment, consisting in the use of two vats, the contents of one vat after having undergone a treatment being discharged into the second vat for renewed treatment, during which proceeding the material is exposed to the air, drawing its advantage in oxygen supply.

The importance of oxygen is fully recognized in the refinement of gold bullion and cyanide precipitates. Mr. Kirke Rose (Inst. of Mining and Metallurgy Adv. Sheets, April 13, 1905), concludes after a series of elaborate experiments that "base metals can be removed from gold and silver bullion by means of a current of oxygen passed through them." Mr. Rose in his experiments used air as well as oxygen gas, and found that air can do what oxygen does, only more slowly and without such intense action, and that it is obviously a cheaper oxidizing agent than oxygen in any other form. The use of pure oxygen, in his opinion, will have to be confined to places where compressed oxygen can be easily and cheaply obtained. Mr. Rose had, of course, not heard of oxone at the time his experiments were concluded, otherwise he would have known that the use of oxygen gas to-day is not any longer confined to places to which the compressed gas can be shipped. And probably some of the audience are not acquainted yet with this new compact oxygen compound called "oxone."

But before directing your attention to this latest offspring of Niagara Falls I may briefly mention the important rôle which

oxygen plays all around in metallurgy—in shaft furnaces, in roasting, in refining and in blast-smelting, as well as in wet processes and, finally, in the regeneration of lyes.

In a report of recent date, signed by the Aachener Institute für Metallhüttenwesen und Elektrometallurgie, practical experiments are described, made in the copper converter process. It was safe to assume that in this process the influence of additional oxygen would be clearly distinctive—and so it was.

The result proved that in using blast air containing 5 per cent. to 9 per cent. above the normal contents of oxygen

(1) The temperature was remarkably raised.

(2) The time of blasting was considerably shortened, viz: to two-thirds and one-half of the time needed with ordinary blast air.

Those interested I refer to the July issue of *Borchers' Metallurgic.*

Now in talking about these processes where oxygen in its molecular form is employed, you may think that I have deviated from my subject, which concerns the use of ozone or active oxygen. But I have not, as the means which I herewith propose for the realization of these long schemed problems is a product which is derived from peroxides, or, it is better to say, which is made of peroxides. It is the above mentioned "oxone."

Oxone is a fused peroxide of sodium prepared to generate oxygen gas instantaneously, upon being immersed in water. While sodium peroxide in its powder form dissolves in water, forming peroxide hydrate or atomic oxygen, not entering the gaseous state, the fused peroxide by heat of dissociation in the instant of solution drives out all its available oxygen. That this oxygen, which is in the molecular form, does contain a certain percentage of ozone, it is fair to assume.

It is found that 1 pound of oxone furnishes on an average 2.15 ft.^{3} oxygen gas at normal temperature and pressure. As the product has a small volume, the gas production amounts to 312 times its own volume, or 130 times the volume of water.

The product is adaptable for shipment to any distance and offers no danger of explosion or combustion, and no inconvenience whatever in the use except the strong causticity, which has to be taken into consideration when handling the same.

The advantages offered by such product are obvious, and the great influence which the presence of such practical, easily transportable oxygen supply will bear upon the development of certain industries is beyond question. The hesitation which most professional men, being fully aware of the value of oxygen, have shown to the use of this gas due to the restrictive and clumsy use of heavy containers of compressed or liquid gas, will at once vanish.

(Follows a demonstration of oxone.)

DISCUSSION.

Mr. Toch: The paper is particularly interesting to me as relating to the bleaching of oils. In a laboratory you can accomplish a great many things which you cannot accomplish successfully on a large scale. The bleaching of linseed oil has made very little progress. I have been at it 19 years and inherited the present process, that is, the addition of a small quantity 50 per cent. sulphuric acid solution and pumping up air into the oil. I worked out the theory of the action and found out that the bleaching of linseed oil is due to the change of chlorophyll into a higher oxide known as xanthophyll, which is merely a change in the coloring substance. You do not extract the coloring matter; you simply change it. The addition of ozone to oil unquestionably does the work much quicker; so in making these experiments, if a very small quantity will do what Dr. Foregger has said, we have undoubtedly come to a very good thing and it will be of commercial importance.

Prof. W. S. Franklin: When Dr. Foregger was speaking of the use of calcium peroxide as an oxidizing agent instead of ozone, I asked my friend, Mr. Brown, why it could not be used for ageing whiskey. He said it might convert whiskey from a soft drink into a hard drink.

Dr. Chas. A. Doremus: It is curious to note how we revert to old work on new lines. When the British Army was to go to Africa means had to be provided—though they did not know much about bacteriology at that time,—for the purification of water. This was done by the use of calcium permanganate, which

is added to the water so long as the salt is decolorized. The treatment was found efficient.*

Calcium permanganate has the formula $Ca\ (MnO_4)_2$, and gives off five atoms of available oxygen, or nearly 30 per cent. of its weight—twice as much as the best of the peroxides mentioned, so that in our old potassium permanganate, which with chloride of lime were the only disinfectants used in the Civil War, we have still one of the cheapest and most efficient sources of oxygen.

We are familiar with the fact that its uses are much the same as those to which the peroxides are put. Tessiè du Motay devised a method of bleaching silk. After the silk is put in a permanganate solution, the brown stain of manganese brown, is removed by dipping the silk in a dilute solution of sulphurous acid. The most delicate tissues may therefore be bleached, at perhaps cheaper rates, by permanganates than by the peroxides. I say it is interesting to see how we revert to what we have long known, and make use of the facts along new lines.

Dr. Foregger: As far as I know, the finest silk bleaching is done nowadays with hydrogen peroxide and sodium peroxide. I would like to hear some expert on silk bleaching tell me to what extent potassium permanganate or calcium permanganate is used in these days.

Dr. Doremus: I said it can be done.

Dr. Foregger: It can be, but it is not done. It can also be used for sterilization, but it isn't, and why isn't it?

Mr. Toch: Calcium permanganate has been used as a bleaching agent for oils, but you cannot keep it. If you had a substance having a formula of $CaO.Mn_2O_4$ and had it in a hermetically sealed glass tube, that would be all right; but you have a hydroxide of calcium which precipitates the black oxide of manganese and instead of being permanent it decomposes itself. I have tried to make that several times.

Dr. Doremus: Of course potassium permanganate which is a perfectly stable substance, may be used.

Why things are not done is very difficult to say. It depends upon commercial enterprise. Thus oxygen was manufactured in New York City, to the extent of filling a holder of 20,000 cubic feet, per day. No such quantity is manufactured anywhere in

* Sir William Crookes, Chemical News, XXVIII, (1873), 244.

the world, so far as I know, now. The enterprise could not be continued, in spite of the fact that the city was piped from 44th Street to Union Square, and the gas delivered along the route.

Things change. What I specially wanted to point out was the highly efficient character of the permanganates.

Dr. Foregger: Yes, and they are therefore extensively used in laboratories, but for commercial use they are not of great value, for certain reasons; one of these reasons is the coloration, and another, because, usually, considerable amounts of sulphuric acid have to be used in connection with them.

Mr. S. S. Sadtler: I might suggest a reason, and that is, that in the case of potassium permanganate you essentially have a wet reagent and in the case of these peroxides the amount of moisture in the oils is about sufficient, I should think, to liberate the oxygen. There is so little peroxide used and traces of water that are in all these oils are probably sufficient to effect the bleaching; while the use of permanganate means the agitation of the permanganate solution with the oil, as two immiscible layers.

Mr. C. F. Carrier: In that experiment something struck me as very peculiar—to draw a parallel case. In the Goldschmidt process, the alumino-thermic process—we use aluminium powder in order to get a quick reaction, and in this case he takes a powdered sodium peroxide and puts it into water and it does nothing so far as you can see; and then he takes a solid sodium peroxide which he says is essentially the same thing and it gives a violent reaction. On the face of it, it is not very easily understood. I am afraid I am probing into commercial secrets now, but from a parallel case I cannot understand why that is.

Mr. Foregger: I will be pleased to give you part of these samples and you may find out yourself if there is any particular secret in it.

Mr. Carrier: Can you explain why the violent reaction takes place with a solid material, and almost no reaction with the powdered?

Dr. Foregger: You heard yesterday that the heat is necessary to liberate the oxygen; and this is a fused material and there is certainly far more heat generated than in the powdered material. It is the heat that produces the liberation of oxygen.

Mr. Sadtler: In confined space?

DR. FOREGGER: The liberation of oxygen is produced by a local superheating caused through the close proximity of the molecules in the fused state. The heat produced by the solution of the peroxide is not sufficient to drive out the oxygen in the gaseous form.

MR. CARRIER: Then by simply fusing that powder you would get a cake, and that would do the same thing as the piece of fused material that you put into the water.

DR. FOREGGER: Yes. A catalytic agent may also be used to hasten the liberation of oxygen. However, this is not necessary, as the generation of gas is slower without the catalytic agent than with it. The principal condition is that the material is fused.

PRESIDENT BANCROFT: I must confess ignorance, but is not the ordinary sodium peroxide a hydrated salt containing eight of water, and is not the difference due to the fused salt being anhydrous?

DR. FOREGGER: No, that could not be, because the ordinary sodium peroxide contains about 97 per cent. peroxide, so there would be very little left for water of crystallization. If a peroxide is dissolved in water or in dilute acids, hydrogen peroxide is formed, i. e., the active oxygen set free from the peroxide combines with H_2O_2, provided nothing is in its way. If, however, the liberated active oxygen comes in contact with organic substance, or, as in our case, if heat acts upon the same, the formation of H_2O_2 does not take place, but the oxygen, being influenced by the medium, reacts upon the same and forms molecular oxygen.

DR. J. W. RICHARDS: I am always interested in the new projects that our electrochemical friends bring forward and which may have important applications. I am interested particularly in the metallurgical applications which are spoken of in the paper: for instance, in the refining of gold and silver and in the oxidizing of other metals. It seems to me that sodium perborate would be one of the best things to use in the fire refining of gold and silver, because the sodium borate remaining after the oxygen was given off would be just the flux which is needed for the production of a fusible slag.

If calcium peroxide could only be cheapened there might be metallurgical uses for it, where lime is now used as a proper slag for the operation. Many endeavors have been made for

increasing the amount of oxygen in the blast supplied to blast furnaces, and that has even been tentatively tried. If calcium peroxide became anywhere reasonably cheap a small amount of that used in place of the lime which is thrown in with the charge at the top of the furnace, if powdered and blown in at the tuyeres with a blast, would increase very noticeably the percentage of oxygen in the blast, and the lime would furnish one of the ingredients of the slag. I can conceive that it might lead to a very great improvement in blast furnace practice—all depending on the cost and the price at which the peroxide could be furnished.

Mr. Fahrig: Dr. Richards has mentioned possible uses in metallurgy and especially in the extraction of gold and silver from ore. I have had very large experience in my own plant and others, and I have found, out of six months' experimenting in active oxygen, the results were against it, and I turned back to the old way of blowing air under high pressure. In fact, I doubted very much that McArthur's is successful on account of his oxygen. Owing to the Siemens process we have there a difference—a great difference: we have not so much active oxygen and yet the Siemens process works very successfully. I am quite sure that I work with air—with the ordinary air, and compressed air—very successfully, and I have tested on a large scale very low grade ore without blowing air, by simply making what we call a Serpentine and letting the product run slowly, giving it from 1 to 1½ in. pitch, which results that the air gets through nicely oxidized by the large surface, and destruction is perfect; and consequently I have come to the conclusion that it is not the active oxygen required in condensed form, but it is a large surface of oxygen required to do the work successfully in the extraction of gold and silver by any cyanide process.

Dr. Doremus: How much does oxygen cost per cubic foot? What is its lowest price when made from any of these substances, per cubic foot, at standard temperature and pressure?

Dr. Foregger: If you speak of oxygen in gaseous form you can of course only consider the oxygen of Oxone, for this is the only compound which furnishes oxygen in that form. There the price will be about fifteen cents per cubic foot. This is a low price for large consumers. As it is a new chemical, just being

introduced, it is impossible to say anything definite about the price. Perhaps the article will be sold much cheaper in a few years.

Of course the price of Oxone cannot be compared with the cost of oxygen sold in iron drums, because as far as I know, the latter is sold at eight or ten cents per cubic foot.

DR. DOREMUS: Twenty cents.

MR. TOCH: Is the oxygen of Oxone sufficiently pure for organic analysis?

DR. FOREGGER: It is about 98 or 99 per cent. pure, the impurity being caustic vapors, which can easily be absorbed by passing the gas through a washing bottle. On the other hand, the compressed oxygen of the tubes, as far as I am informed, is only about 90 per cent. pure.

MR. SADTLER: I have not found it that good. I have found it about 75 per cent. pure.

DR. FOREGGER: Exactly.

PROF. SCHOBER: Is there any possibility of the oxygen as it comes out of the generator here, containing any appreciable percentage of carbon dioxide?

DR. FOREGGER: It is simply impossible for it to contain carbon dioxide, because any carbon dioxide would be absorbed by the sodium lye which is formed by the solution, and this is one of the great features of the product. It belongs to another chapter, which I did not mention, that this compound has the property not only of generating oxygen, but of absorbing carbon dioxide.

It is a known fact that sodium lye absorbs carbon dioxide, and the capacity of the Oxone solution in this respect is by far greater than its capacity for generating oxygen. I have made experiments in that direction and find that it is hard to saturate the solution with carbon dioxide. On this account, for the purification of air in public rooms, hospitals, etc., and for the navy, in submarine boats, the product would prove of great value.

A piece of Oxone represents the functions of a plant,—in furnishing oxygen and absorbing carbon dioxide. If you expose a cake of Oxone in a room it will last about 12 or 14 days before it is decomposed by the moisture of the air, and I find

that during that time about 90 to 100 c. c. of oxygen was generated per hour.

Dr. Doremus: I want to get one thing very straight in the gentlemen's minds. We need a double molecule of potassium permanganate to get five atoms of available oxygen. We know that it gives off oxygen under very little provocation; put into foul water it will be immediately decolorized. Mr. Langmuir cites a case where permanganate and glycerine produced a spontaneous combustion. The fire started on a truck loaded with packages of permanganate and barrels of glycerine while the truck was on a ferry-boat going to Brooklyn. The truck had to be thrown overboard. Sponge placed in permanganate solution turns brown, and this brown color can be removed by sulphurous acid solution, the permanganate has been reduced, oxidation has taken place and the sponge has been bleached. The same happens with silk, so that the most delicate fibers may be bleached without the aid of sulphuric or other acid to free the oxygen.

The advantage of the calcium permanganate is that for each $Ca = 40$, we should have $2K = 2(39.1)$. If this salt were properly made I think there would be no difficulty in keeping it.

Now, unquestionably, for the production of oxygen *in situ*, these peroxides, the permanganates and some other products, are very proper, but I cannot see that we have made any great chemical advance in the production of oxygen gas to be used as a gas on a large scale. Gas from these peroxides is somewhat cheaper than that made from potassium chlorate which costs from $150 to $200 per 1000 cubic feet. According to Dr. Foregger compressed oxygen is worth about $80 per thousand. Gas at such figures is out of question for manufacturing.

One of the first important processes for obtaining oxygen was that of Tessiè du Motay. An interesting experimental apparatus was constructed in 1869 in the following way. An iron tube, about 1½ inches in diameter, such as can be put in an ordinary laboratory gas furnace, was filled with lump sodium manganate, Na_2MnO_4, and discs of sheet iron were interspaced to force the air up and down, in a zig-zag fashion, through the manganate. The tube was capped and fitted with inlet and delivery tubes. When steam is blown through, the heated manganate yields oxygen; when air is blown through, oxygen is ab-

sorbed and the manganate reformed. This apparatus has been used each year in experimental demonstration, though never recharged.

It has been calculated that where steam and coal are cheap, oxygen should be produced by this process at the rate of 50 cents per thousand cubic feet.

DISCUSSION.

(Communicated after adjournment.)

Dr. Foregger: I feel obliged to Dr. Doremus for his explanation as I consider the same an historical illustration of the progress which is being made in the chemistry of oxidation. To enter any further into the subject would carry me too far back into fields we have already passed through.

I will, however, mention that Dr. Doremus is making a slight mistake in stating that in the decomposition of potassium permanganate in water, without the addition of sulphuric acid, a double molecule, permanganate yields 5 atoms of available oxygen. This reaction is as follows:

$$2\,KMnO_4 + H_2O = 2\,MnO_2 + 2\,KOH + 3\,O.$$

2 molecules of permanganate yield, therefore, 3 atoms of active oxygen, or 15.2 percent.

The process of bleaching with permanganate, as described by Dr. Doremus, sounds easy, but, as it stands, is not very explanatory.

The reasons why permanganate is used for silk bleaching are, the detrimental action of the caustic potash which is formed and of the sulphurious acid, or the sulphite, which has to be employed.

Similar reasons stand for the non-employment of permanganate for sterilizing drinking water. Caustic is of no advantage to our system, and the black manganese oxide formed is a cumulative poison. There is no doubt that with calcium or magnesium peroxide no toxic by-products are involved by using them for sterilizing water.

Now, for the production of oxygen in situ, I will say that "these peroxides, the permanganates and some other products," are not at all "very proper;"—by the solution of these chemicals atomic oxygen is formed, and in no instance, gaseous oxygen. Dry heat would produce oxygen gas, but that could hardly be considered a production in situ—at least, not a very convenient one.

For the production of oxygen in situ, fused sodium peroxide "Oxone" is, in the present day, the best means available, as it works automatically, in producing the gas by mere contact with water.

I have not heard of any such reaction of permanganates, or other products—though I do not doubt that an invention in the line indicated by Dr. Doremus could be made.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 19, 1905, President Bancroft in the Chair.

REPORT ON THE PROPOSED CARD CATALOGUE OF ELECTROCHEMISTRY.

By Mr. C. F. Carrier, Jr.

It is not necessary to explain the value of a card index, because every one here is familiar with its use. The idea of the Concilium Bibliographicum is to publish a complete bibliography of electrochemistry. They start at the beginning of 1906 and will review every current periodical and index everything that appears on electrochemistry, patents, research work, etc., and ultimately they hope to begin at January, 1906, and work backward; then the science will be completely indexed.

Then, in addition to having a complete index, they have devised a system of classification, so that one can get at these references after they have been obtained. The Concilium has access to all the periodicals which are taken in the libraries of Switzerland, and thus have some 30,000 periodicals at their command. They are subsidized by the Swiss government, so that any periodicals not obtainable from Zurich, they can obtain from any other public library in Switzerland. This includes nearly all the periodicals in the world which are apt to have anything in regard to electrochemistry.

The value of such an index depends on thoroughness. If a person is going to depend on a bibliographic institute for their references they must feel sure that it has been complete, and from my personal association with Mr. Voege I know positively that his work is going to be thorough and complete. He has given his time and has gone into it thoroughly—so thoroughly, in fact, that it has been delayed almost two years in appearing since he first undertook it.

I understand that the Board of Managers of our society have decided to have a complete edition of these cards on file in the office of the society. It is not necessary for any person to subscribe for the complete edition, and I want to lay special emphasis on that

one point, because at the start there will probably be 5,000 cards a year, and no one will be interested in all the varied branches of electrochemistry, but they can subscribe for any one single branch that they want.

Suppose a man is only interested in electric furnaces, plating, storage cells, the manufacture of chemicals, or electrolytic refining: any one branch can be subscribed for by itself and the cost of the cards will depend upon the number which are purchased. If the complete edition is purchased the cards will not cost over a half a cent apiece; but if only about 100 to 200 cards are purchased, they will cost as high as 3 cents apiece, depending entirely upon the number.

The Code—that is, the systematic plan of classifying these cards—is an elaboration of the Dewey system, and is based on subdivision by decimal numbers. This has now been published and is on sale. The price of the code is 50 cents, and up to the present time only the numerical code is ready, but with each numerical code is a postal card, which, upon being returned to the Concilium Bibliographicum, entitles the purchaser of the decimal code to the alphabetical code free of further charge.

The objection has been raised to this system that it is so complicated that no one but a trained bibliographer can use it. This is not true, because there is an alphabetical code going with it, and anything which cannot be found by the numerical arrangement, can immediately be located in the alphabetical index and its number found.

DISCUSSION.

Dr. Waldo: This card catalogue is a very important matter. Most of us depend on our card catalogues. The Library of Congress issues a card which is cut to the size of the Library Bureau of Boston from which Bureau most of us get our supplies. So it is extremely important that these foreign cards be cut to that size if they are going to be used to any extent in our current card catalogues, and those of us who have card catalogues running to five and six thousand titles know what an incubus it will be to have differing sizes of cards for card catalogues.

When indexers set out to index periodicals they generally omit those transactions which are not for sale and which are published for members of societies: take for instance the minutes of the proceedings of the Institute of Civil Engineers. They are seldom independently indexed, for the reason that the volumes are not for sale, are issued only to members and do not pass under current review. The Journal of the Iron and Steel Institute is similarly placed, so that unless those papers happen to be reprinted—or some abstract or review is elsewhere published in current technical papers—they are omitted. I think if we could in any way impress upon the foreign publishers that we have a standard size of card generally used in the United States; if in addition these cards issued for the United States would be of that standard size; and if, furthermore, there was some assurance that in what are called "Periodical lists," the discussion of the great technical societies were to be indexed—it would add very much, indeed, to the value of this system. Those two points are extremely important—the size of the card and the fact that those transactions not on general sale should be indexed.

Mr. Carrier: These cards are all cut to the standard American library sizes, 12½x7½ centimeters, and are punched for the rods of standard card drawers. The centimeter size varies by something over a millimeter from the standard American card.

This European card cut in the metric scale varies by a little over a millimeter from the American scale, so that it is a little bit smaller.

Dr. Waldo: Absolutely useless!

Mr. Carrier: In regard to the indexing of the periodicals, a complete list of all periodicals will be indexed, and if by any chance such periodicals as mentioned by the last speaker should be omitted, a person subscribing for the index will know what is omitted. Every periodical in the list will be thoroughly indexed. Such periodicals as are not obtainable in Switzerland will, of course, be omitted; but the list will include everything which is indexed.

President Bancroft: I think it would probably be safe to go farther than Mr. Carrier does. Mr. Voege is a graduate of Cornell University and I think there is no question but that if his attention is called to the absence of any periodical from the

list, he will at once take steps to include it. Not being especially familiar, myself, with the uses of a card catalogue, I have not realized that a difference of a millimeter would play havoc with things; but I think, under the circumstances, since the first edition does not begin until January, it would be very desirable for Mr. Carrier to call Mr. Voege's attention to that difference, and to see whether it would not be possible to have the cards made exactly of standard sizes in this country. It would largely be a question whether more cards would be sold in this country or abroad; and the standard should be made to fit. We are very much indebted to Dr. Waldo for bringing out this point.

Dr. Doremus: I would add that all cards of a size are not alike. There are some which are cut in so peculiar a way that they are extremely easy to handle, and others that are exactly the same size but cannot be handled at all well, so that it is not only the question of the size but how they are cut to that size which must play a very important part in the practical carrying out of this scheme.

President Bancroft: I think every one would agree that a card catalogue which did not include the publications of the leading scientific and technical societies would be most emphatically a waste of time; and I feel certain that no such omission is intended by Mr. Voege. If by accident such omission occurs, it will be rectified at once when his attention is drawn thereto. I cannot conceive of any body wishing to subscribe to a set of cards if many of the more important papers are left out.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 19, 1905, President Bancroft in the Chair.

SOME OBSERVATIONS ON THE INFLUENCE OF ARSENIC IN PICKLING SOLUTIONS.

By Charles F. Burgess.

A sulphuric acid pickle which exerts a vigorous dissolving action upon an iron or steel surface may be rendered almost completely inert by the addition of a small amount of arsenic. Over a half century ago this fact was pointed out by E. Millon,[1] who, however, did not attempt to explain why a trace of arsenic has the property of exerting this remarkable protective action.

This phenomenon is of considerable significance to the chemist and the electrochemist, for it indicates that arsenic is a disadvantageous impurity where free and rapid action of sulphuric acid upon iron is desired; that its presence may be advantageous when the rapidity of the action of the acid is to be diminished. Millon claims that arsenic in acids other than sulphuric reduces their activity in corroding various metals, and assuming this to be true, may it not be expected that arsenic when present as an impurity in the metals themselves may render them less susceptible to corroding influences in general?

The writer has been unable to find that the attention has been given to the study of this subject to which its suggestiveness and usefulness entitles it. In what manner does arsenic render an iron surface passive is possibly a question for the electrochemist to answer, and any suggestions or information bearing upon this point will be welcomed by the author.

Some preliminary experiments upon the effect of arsenic in sulphuric acid solutions have been done in the Applied Electrochemistry Laboratories of the University of Wisconsin, some of the results of which are here given.

A five normal solution of sulphuric acid was used in the various tests, and to a portion of this solution was added a small quantity

[1] Comptes Rendus, 1845 *22*, 37.

of arsenic in the form of As_2O_3. Although the exact quantity was not determined, it was present only as a small part of 1 per cent. To determine quantitatively the influence of the pure solution and that containing arsenic, strips of spring steel were subjected to their action, and the dissolving and the weakening of the steel measured. The steel ribbon used consisted of a high grade of untempered spring steel, carrying a thin film of black scale, and having a cross section of 5-16 x .16 inch. From this, pieces about one foot in length were cut, and these were immersed for a depth of six inches in the respective solutions.

Table I gives results on the dissolving effect of the acids upon strips which had been freed of scale by rubbing with fine emery.

TABLE I.

Dissolving effect of acids with and without arsenic.

Time	Pure Acid Solution		Loss	Solution Containing Arsenic		
	Wt. Before	Wt. After		Wt. Before	Wt. After	Loss
20 min.	5.1628 g.	5.1156 g.	.0472 g.	5 0342 g.	5.0290 g.	.0052 g.
40 min.	5 1156 g.	4.9096 g.	.2060 g.	5.0290 g.	5.0268 g.	.0022 g.
60 min.			.2532 g.			.0074 g.

The facts to be noted from this table are that in one hour's time the amount of iron dissolved by the arsenic free solution is about 34 times that dissolved by the impure solution; also that during the first twenty minutes the ratio between the action of the two solutions was 9.1 to 1; and during the last forty minutes the ratio increased to 94 to 1, showing that the protective action of the arsenic increases with the time. In the pure solution the rate of corrosion increases, as shown by the fact that over four times as much iron was dissolved during the last forty minutes as during the first twenty; while with the solution containing arsenic the rate of solution materially decreased. It was also noted that the steel when first immersed in the impure solution liberated hydrogen, but this evolution quickly diminished, and at the end of one hour the evolution of hydrogen had ceased, while in the pure acid the evolution of this gas was vigorous and undiminished.

It is well known that acid solutions exert a harmful influence on steel, aside from that occasioned by the removal of some of

the metal. This is supposed to be due to the liberation of hydrogen and the absorption of it by the metal, rendering it weak and brittle. So marked is this effect that certain classes of steel articles, such as steel piano wire, clock springs, measuring tapes and the like cannot be pickled, and it is claimed by some that they cannot be nickel plated without damage.

To determine whether arsenic exerts an influence harmful or otherwise upon this weakening property of acids, a small testing machine was devised by means of which the brittleness of a strip of steel could be approximately determined.

The steel strip to be tested rests on fixed edges, spaced one-half inch apart. The movable edge is advanced slowly and steadily by means of a micrometer screw until the strip snaps in two, and the deflection thus measured is taken as an approximate indication of the flexibility.

Inasmuch as the steel strip showed variations in its flexibility on samples taken from various places in the coil, measurements were made on the pickled and unpickled portions of each sample tested. The results of observations are given in Table II, the column marked "Per cent. weakening" being derived by dividing the decrease in deflection after pickling by the deflection of the unpickled part.

TABLE II.

Solution	Time	Deflection		Per cent. Weakening
		Pickled	Unpickled	
Pure	5 minutes	.100″	.152″	
		.094	.156	
		.088		
	Ave. . .	.094	.154	39.
With Arsenic	5 minutes	.156	.156	
		.152	.156	
		.154		
		.154		
		.158		
	Ave. . .	.155	.156	0.64
Pure	10 minutes	.080	.170	
		.070	.160	
		.066	.158	
		.078		
	Ave. . .	.074	.163	54.5
With Arsenic	10 minutes	.150	.170	
		.152	.166	
		.158	.170	
		.154		
	Ave. .	.154	.169	8.9
Pure	15 minutes	.062	.158	
		.054	.158	
		.066		
	Ave. . .	.061	.158	61.4
With Arsenic	15 minutes	.142	.150	
		.150	.160	
		.152		
		.154		
	Ave. . .	.149	.155	3 87
Pure	60 minutes	.060	.160	
		.056	.140	
		.050	.160	
	Ave. . .	.056	.153	63 5
With Arsenic	60 minutes	.158	.178	
		.160	.174	
		.154	.172	
		.160		
		.160		
	Ave. . .	.158	.175	9.7

It will be noted that arsenic exerts a marked influence in diminishing the rotting effect of the sulphuric acid solution. A solution of hydrochloric acid having a corresponding strength was also tested, and it was found that while the presence of arsenic in it exerts an influence similar to that exerted in sulphuric acid, its influence is not as pronounced.

It is generally recognized that the nickel-plating process, as usually operated, has a decided weakening effect on thin steel springs and the like, and the supposition is justified that it is the pickling part of the process that is largely responsible for the trouble. To determine whether a steel spring pickled in an arsenic containing pickle and subsequently nickel-plated would be stronger than when pickled in pure acid before plating was the purpose of measurements, the results of which are given in Table III.

TABLE III.

	Deflection.		Per cent. weakening
	Before pickling	After plating	
Pickled in pure acid and nickel plated.	.172″	.140″	
	.172	.154	
		.140	
		.144	
		.148	
Average . . .	.172	.145	15.6
Pickled in acid containing arsenic and nickel plated.	.160	.158	
	.168	.158	
	.172	.154	
		.146	
		.158	
		.154	
Average . . .	.167	.155	7.2

All the above experiments show that the effects of arsenic are sufficiently pronounced to warrant a further experimental study, especially in determining quantitatively the influence of varying percentages of arsenic in various strengths of acid solutions. Such information will undoubtedly be of direct practical value to the electro-plater and others who have to do with pickling solutions.

That arsenic exerts an influence to be reckoned with has been recognized for some time by users of sulphuric acid solutions. By

some it is held to exert a deleterious influence; that its presence in a pickle gives rise to dark and irregular colorations on the surface of iron articles subjected to its influence, thus adding to the many difficulties inherent in the process of preparing surfaces for receiving electro-deposits. Another disadvantage attributed to arsenic is that it makes the useful action of the solution exceedingly slow. On the other hand, it is claimed by Meurice[1] that the presence of arsenic may be decidedly advantageous to an acid pickle, since when present in suitable proportion it reduces the consumption of acid while increasing the effectiveness of its work.

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DISCUSSION.

Mr. Hering: It occurred to me that there might be several explanations of this action. What we generally term iron, is not iron at all, but is a mixture of three things: iron, carbon and carbide of iron; and one reason why it dissolves in sulphuric acid is because those ingredients form electrolytic couples, causing local currents. If that is the case, any arsenic in the solution will probably be plated onto the carbon; hence the local electrochemical action which dissolves the iron, will be weakened by this change of one electrode from carbon to arsenic. This might be one explanation. Whether arsenic will deposit on iron the way copper does from copper solutions, I do not know, but if it does, this might be another explanation, as we know that if iron is placed in sulphuric acid containing copper sulphate, it will at once be covered with copper and will then be less rapidly attacked than if not covered with copper.

The paper furthermore suggests to me that possibly this action might be made use of advantageously in coatings for protecting iron, that is, to protect iron against being attacked by rust or by liquids; it might be quite possible that the use of arsenic in such protecting compounds would be effective.

[1] Bull. de l'Assoc. Belge. Chimistes, *9*, 343, abstracted in "The Metal Industry," Aug., 1903.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 19, 1905, President Bancroft in the Chair.

THE ELECTRIC SMELTING OF ZINC.

By Oliver W. Brown and William F. Oesterle.

Much attention has been given to the reduction of zinc ores, by electrical and other means, during the last few years. This is not surprising when one realizes that the ordinary zinc smelting process is the most wasteful metallurgical operation used industrially at the present time. The fuel consumption, the cost of repairs and the loss of zinc are very large. The average life of the retorts used in many works is only forty to fifty days; while the loss of zinc is seldom less than 10 per cent., and sometimes more than 25 per cent. of the zinc in the ore.

Another great drawback to the process is that the retorts will hold only about 65 pounds of ore. The zinc retorts most commonly used are fire-clay tubes about four feet two inches long, eight inches in diameter and 1¼ inches thick. They are made closed at one end, and into the mouth of each retort is fitted a fire-clay condenser. They are supported at each end by projections from the walls of the furnace; and are placed in horizontal rows in the furnace in such a manner that the flames entirely surround them while they are being heated.

The most important zinc ore is the sulphide, and this ore, before distilling in the retorts, must be roasted for about forty-eight hours in a separate roasting furnace to convert it into an impure oxide. One to two per cent. of the zinc in the ore is generally lost by volatilization during the roasting process; and the roasted ore still contains one to two per cent. of sulphur, which keeps back an equivalent amount of zinc in the retorts.

The roasted zinc ore is mixed with coal and coke, and charged into the previously heated retorts. The retorts and contents are then heated for about twenty hours, up to a white heat. The zinc oxide is reduced to metal by the white-hot carbon, or carbon monoxide, and distills down into the fire-clay condensers, where

it condenses, in part as a fine powder and partly as fused metal. The reduction temperature of zinc oxide, as shown by the work[1] of W. McA. Johnson, is about 1,033° C.; however, all of the zinc will not be expelled from the retort below a white heat. The molten metal is generally drawn from the condensers into a ladle three times during the distillation. Some of the zinc vapor passes through the pores and cracks of the retorts and is lost, while the fire-clay retorts themselves often absorb as high as 15 per cent. of their own weight of metallic zinc. A part of the metal remains in the charge after distillation, because the retorts can not be heated to the temperature required to expell all of the zinc without cracking or melting them. The charge from which the zinc has been distilled generally contains at least 2½ per cent. of metallic zinc, and often much more than this amount. Only pure ores can be used, as the iron and calcium in low-grade ores form a very corrosive fusible slag, which corrodes through the retorts at a comparatively low temperature. The retorts can not be made much longer or wider than those used at present and still hold up their own weight and that of the charge, when heated to a white heat.

As crude and wasteful as this method is, it is employed to produce nearly all of the zinc used at the present time. The enormous amount of heat wasted during the smelting of zinc ores, the loss of zinc, and the cost of operating this process, has caused the problem of the extraction of zinc from its ores to be a favorite field of research with many investigators.

Electrochemists have attacked this problem along three different lines, namely, the conversion of the zinc in the ore into a salt soluble in water and the subsequent electrolytic precipitation of the metal from an aqueous solution; conversion of the zinc to chloride and the electrolytic separation of the metal from the anhydrous fused salt; and the electric smelting of zinc ores.

A special endeavor has been made to develop electrical processes by which zinc can be economically extracted from complex and low-grade ores, which can not be smelted in the ordinary manner.

Of all the processes which have been suggested, involving the electrolytic precipitation of zinc from aqueous solution, that

[1] Trans. Amer. Electrochem. Soc., 5, 211 (1904).

developed by Hoepfner is the only one that appears to have approached a commercial success. Brunner, Mond & Co. have during the last few years turned out a very pure electrolytic zinc from their works at Wilmington, near Chester, England. Little is known concerning the details of their process except that it is based on the Hoepfner patents.

The Hoepfner process was also used in a works located at Fuhrfort, Germany, from 1895 to 1897, but it has been discontinued. In this works metallic zinc and chlorine were produced by the electrolysis of a solution of zinc chloride. The chlorine was converted into bleaching powder. A description of this process has been published by Guenther.[2] It seems that its success was not great. The large amount of power required to precipitate zinc from aqueous solutions will always be one of the greatest hindrances to any process of this kind.

Many electrochemists have believed that the treatment of low-grade zinc ores could be successfully accomplished by a process in which the zinc is separated by the electrolysis of some anhydrous fused salt of zinc, like the chloride. Richard Lorenz, Borchers, Swinburne, Ashcroft and others have endeavored to develop processes for zinc extraction depending on the electrolysis of fused salts. In this field the Swinburne-Ashcroft process[3] seems to be the best and to have a very bright future.

Few trials in the electric smelting of zinc ores were made until within the last few years, although the Cowles Bros., of Cleveland, carried out experiments on the smelting of roasted zinc ores by electrical heating as early as 1882. These early experiments did not lead to a commercial process.

C. Casorette and F. Berboni,[4] of Milan, Italy, have invented a furnace for smelting zinc ores which contains two muffles, the second being heated by electrical means.

An electric arc furnace for smelting zinc ores has recently been invented[5] by Dr. C. F. T. de Laval. In his furnace the pulverized zinc ore, mixed with the proper reducing and fluxing

[2] Eng. and Mining Journal, May 16, 1903.

[3] Chlorine Smelting with Electrolysis, James Swinburne, Electrochemist and Metallurgist, *3*, 68 (1903).

[4] Zinc Smelting, C. Casorette and F. Berboni, Milan, Italy; British Patent No. 472, May 19, 1900. Eng. and Min. Jour., *76*, 163 (1903).

[5] French Patent No. 325,895, Oct. 21, 1902. U. S. Patent granted to Dr. de Laval, August 29, 1903.

materials, is fed into the top of an electric furnace in such a manner that in descending it presents an inclined surface to the heat radiated from an arc. The zinc vapors are conducted to a condenser, while the gangue as it descends into the lower part of the furnace is fused and is drawn from the furnace in the molten condition. It is claimed that in smelting 40 per cent. zinc ore in a 100 kw. furnace, nearly five kgs. of metallic zinc are produced per kw. day.

The Cowles Bros., Casorette and Berboni, and de Laval have tried to design electric furnaces in which roasted zinc ores could be smelted in the ordinary manner, except that the heat be generated by electrical means.

A. Dorsemagen,[6] of Wesel, Germany, has worked out a process in which he smelts a zinc ore in an electric furnace with the simultaneous production of a valuable by-product. His process is designed for the treatment of zinc silicate ores. He mixes a zinc silicate ore with carbon in proportions indicated by the reaction $Zn_2SiO_4+5C=2Zn+SiC+4CO$, and heats the charge in an electric furnace. The zinc distills out and is condensed in the usual manner, while the silicon of the ore combines with carbon, forming carborundum. The inventor claims the advantages of supplying the heat required for the reduction of the zinc ore and the formation of silicon carbide at the same time, thus reducing the loss of heat due to radiation and the amount of heat required to previously heat the reacting materials.

If a process were devised to electrically smelt unroasted zinc sulphide ore, the advantages of electrically heating the charge could be realized, while at the same time all the cost of roasting the ore could be saved. After experimenting for about two years on the extraction of zinc from its ores by electrolysis of fused salts and of aqueous solutions, the writers attempted to find such a process. We have obtained interesting results from a process[7] based on the electrical smelting of charges of unroasted zinc blende, lime and carbon, mixed in proportions corresponding to the following equations:

$$(a) \quad 2ZnS + 2CaO + 7C = 2Zn + 2CaC_2 + CS_2 + 2CO,$$

$$(b) \quad 2ZnS + CaO + 4C = 2Zn + CaC_2 + CS_2 + CO.$$

[6] U. S. Patent No. 716,008, Dec. 16, 1902.

[7] U. S. Patent No. 742,830, Nov. 3, 1903. All of the experiments carried out jointly by Oesterle and Brown were performed in the electrochemical laboratory of Indiana University.

Before giving any of the results of our work we wish to refer to the process patented[8] by Paul Dankwart, of Deadwood, S. D. The process described by Dankwart is similar in some respects to that employed by us. Dankwart smelts mixed sulphide ores containing zinc, with lime, coke and sodium sulphate. He mixes the different materials in such proportions that the sulphur of the ore is converted into alkaline and alkaline earth sulphides, while the zinc is liberated as vapor and is condensed in the usual manner. Dankwart's process is very similar to that of Kirkpatrick-Picard,[9] of London, except that Dankwart adds sodium sulphate to the charge of sulphide ore, lime and carbon, used by Kirkpatrick-Picard, and also carries out his process in an electric furnace.

Kirkpatrick-Picard's process is represented by the following reactions:

$$ZnS + CaO + C = Zn + CaS + CO$$
$$PbS + CaO + C = Pb + CaS + CO$$
$$4ZnS + 2Fe_2O_3 + 6C = 4Zn + 4FeS + 6CO$$
$$4PbS + 2Fe_2O_3 + 6C = 4Pb + 4FeS + 6CO.$$

He forms the mixture into briquets before the distillation.

The writers first tried the reduction of a charge containing equal molecular weights of zinc blende (59.6 per cent. zinc in ore) lime and carbon (coke) in an enclosed electric resistance furnace lined with firebrick. This is the same charge as that used by Kirkpatrick-Picard. When this charge was heated in the electric furnace the ore was readily reduced, the metallic zinc distilled out and a portion of it condensed in an iron tube which served as condenser. The material remaining in the furnace after the distillation, consisting of impure fused calcium sulphide, contained only 0.13 per cent. of metallic zinc.

We next made a study of the electric reduction of charges of zinc blende, lime and carbon (coal or coke), mixed in proportions corresponding to the equations (*a*) and (*b*) given above.

When a charge containing 194 grams of zinc blende (59.6 per cent. zinc), 112 grams of lime and 84 grams of coke was heated in an enclosed firebrick lined electric resistance furnace, with a current of 50 ampères at 30 volts for two hours, zinc distilled and

[8] Process of Recovering Zinc from Sulphide Ores, P. Dankwart, U. S. Patent No. 746,798, Dec. 15, 1903.

[9] U. S. Patent No. 692,148, Jan. 28, 1902.

condensed, and the impure carbide remaining in the furnace contained only 0.036 per cent. of metallic zinc and 2.89 per cent. of sulphur. The other impurities in the carbide naturally depend on the purity of the ore treated.

When working with the very small furnace required to smelt charges containing only 194 grams of ore, it was not deemed desirable to endeavor to condense the largest possible proportion of the distilled zinc in a solid metallic form. As experience has shown, the difficulties in condensing the zinc as liquid metal, instead of zinc dust, disappear as the size of the furnace is increased.

The analyses of gases coming from the furnace during the operation, of the materials in the furnace after smelting, etc., show that the changes which take place in the smelting are probably best represented by equations (*a*) and (*b*).

Some additional experiments which were carried out during 1903 and 1904 by one of the writers[10] on the reduction of zinc blende, furnished the following results:

When the following charge: 3.98 kg. zinc blende (containing 58.0 per cent. of zinc), 2.24 kg. lime (containing 38.2 per cent. of magnesia), 0.84 kg. of carbon (equal weights of coal and coke), was smelted in an enclosed electric resistance furnace, the material remaining in the furnace after the distillation contained only 0.10 per cent. of metallic zinc. This experiment shows that even when a lime very high in magnesia is used, practically all of the zinc is reduced and distills out of the furnace. However, it is hardly necessary to remark that good calcium carbide can not be made when a lime containing 38 per cent. of magnesia is used.

The internal dimensions of the furnace in this experiment were: length, 12.5 inches; depth, 8.5 inches, and width, 4.5 inches. The inner walls and bottom of the furnace were of magnesia brick. A layer of dry lime was placed on the outside of the magnesia brick, then a layer of firebrick, followed by another layer of lime, and finally the whole was encased in a sheet-iron jacket. A round Acheson graphite electrode, two inches in diameter, entered the furnace at each end. These electrodes were fastened firmly into plates of Acheson graphite 0.5 inch thick, which were placed vertically at each end of the furnace, and reached from the bottom

[10] Brown, Laboratory of Applied Electrochemistry, University of Wisconsin.

to within 1.5 inches of the top. In order that the furnace should be gas tight, the portions of the graphite electrodes which passed through the walls of the furnace were packed in powdered magnesia brick.

The materials comprising the charge were passed through a 20-mesh sieve and thoroughly mixed, before placing in the furnace.

Connection between the two end electrodes was made by two cores of broken carbons (broken to pieces about 0.5 to 1 inch), which were imbedded in the charge. The lower core of granular carbon was placed 2 inches from the bottom of the furnace, while the second core was about 4 inches above the lower core.

The charge was filled into the furnace to within 1.5 inches of the roof, and was covered with a layer of broken pieces of coke. A carbon tube, 0.5 inches internal diameter and 12 inches long, penetrated the side wall of the furnace, about 2 inches from one end and 2 inches from the top. The tube passed nearly horizontally through the walls of the furnace, the outer end being about 0.5 inch lower than the inner. On the outer end of this carbon tube was fastened a short piece of 1.5 inch iron pipe, which was surrounded with asbestos, and served as condenser for the zinc. The outer end of the pipe was nearly closed with fire-clay. At intervals during the distillation of the zinc the fire-clay plug was removed and the melted zinc, which had condensed, was allowed to flow out.

The furnace was closed at the top by an Acheson graphite plate, 0.5 inch thick. A layer of lime was placed over the graphite plate, and on this were placed three layers of fire-brick. When the furnace was sealed with dry powdered lime in this manner it was quite tight, and very little gas escaped except through the condenser.

A current of about 172 ampères and 68 volts was passed through the furnace for six hours and forty minutes. Zinc vapors had stopped coming from the furnace when the current was broken.

After the furnace was allowed to cool and the cover removed, it was found that the charge was a loose porous mass, which could nearly all be removed with the hands. The temperature had not been sufficient to fuse the charge, although all but 0.1 per cent. of the zinc was expelled from the furnace.

In order to gain some idea of the temperature required to reduce and distill the zinc from various charges, and also the relative value of various charges, four different mixtures were made up and heated in a hot coke fire in a wind furnace.

The materials in each charge were pulverized to pass a 20-mesh sieve and well mixed. The blende used contained 58.6 per cent. of metallic zinc. The charges were as follows:

No. 1 contained zinc blende, 97; lime 28, and coke, 24 grams, and corresponds to the equation,

$$2ZnS + CaO + 4C = 2Zn + CaC_2 + CS_2 + CO.$$

No. 2 contained zinc blende, 97; lime 56, and coke, 42 grams, and corresponds to the equation,

$$2ZnS + CaO + 7C = 2Zn + 2CaC_2 + CS_2 + 2CO.$$

No. 3 contained zinc blende, 97; lime 56, and coke, 12 grams, and corresponds to the equation,

$$ZnS + CaO + C = Zn + CaS + CO.$$

No. 4 contained zinc blende, 97; silica 120, and coke, 24 grams, and corresponds to the equation,

$$2ZnS + SiO_2 + 4C = 2Zn + SiC + 2CO + CS_2.$$

The four charges were placed in separate assay crucibles, loosely covered, and placed in a hot coke fire. Charges 1, 2 and 3 were heated two and three-fourth hours, while charge No. 4 was heated two and one-sixth hours. A zinc flame burned from the mouths of crucibles 1, 2 and 3 while they were being heated, but no zinc flame was given off from crucible containing charge No. 4, indicating that no reduction took place in No. 4.

An analysis of charges 1, 2 and 3 after heating showed that about 55 per cent. of the zinc had been reduced and volatilized in each case. A practically complete reduction and volatilization of the zinc takes place when either charge 1, 2 or 3 is heated in an enclosed electric furnace, with a current of 50 ampères and 30 volts for two hours or less.

Only 5 per cent. of the zinc in charge No. 4 was lost during the heating. This loss was probably due to mechanical loss in removing the ignited charge from the crucible after firing.

A charge made up in the same proportions as in No. 4, but containing zinc blende, 194; silica 260, and coke, 48 grams, was

heated in an enclosed electric resistance furnace for one hour, with a current of 120 ampères and 50 volts. Only a very small amount of metallic zinc (about one gram) was found in the condenser, and an analysis of the powder which collected in the condenser showed that it contained only about 4 per cent. more metallic zinc than the charge which was placed in the furnace. The material remaining in the furnace after heating contained 3.98 per cent. of metallic zinc.

These data show that zinc sulphide is not reduced to metal when mixed with silica and carbon and heated to a very high temperature. The temperature attained in this experiment was high enough to volatilize most of the charge out of the furnace, yet the zinc ore was not reduced to metal.

Attention has often been called to the fact that processes requiring widely different conditions can not be successfully carried on together. This is probably very true of the production of zinc and calcium carbide. The conditions required for the reduction of zinc and the production of calcium carbide are so different that there is little chance for their simultaneous economic production. Even if many of the drawbacks could be overcome, the production of a sulphur free carbide from a charge of zinc sulphide, lime and coke, is most probably impossible. Also, if calcium carbide is to be made as a by-product, only the purest zinc sulphide could be smelted, as all of the impurities in the ore would contaminate the carbide. However, a method of smelting high-grade zinc ores is not needed so much as a process which will economically obtain the zinc from ores high in iron, etc.

Another disadvantage in the production of zinc and carbide in the same operation is that the sulphur can not be recovered in a suitable condition, as the greater portion of any carbon disulphide which may be formed in the reduction is burned to sulphur dioxide, which escapes from the furnace in a highly diluted form.

Two very promising lines of investigation are open to those who wish to find an economical electric method of smelting zinc ores. Roasted zinc ores may be smelted in the electric furnace, with coal or coke, and just enough other material to form with the impurities an easily fusible slag which may be continuously tapped from the furnace. Electric smelting under these conditions has the advantage over the ordinary method in that it may

be made entirely continuous; that the walls of an electric furnace can be easily constructed of materials which are impervious to zinc vapors and which will not be corroded by the slag, thus enabling the temperature to be raised to a point at which all of the zinc will be expelled from the ore; and that the heat is applied internally, thus preventing the large waste of thermal energy occurring in the ordinary smelting process. Ores high in iron and other impurities could be easily smelted, as the walls of an electric furnace can be made of materials which will withstand the corrosive action of the slags.

It seems possible that zinc sulphide might be economically smelted in the electric furnace, without a preliminary roasting, if ore, lime and carbon be mixed in proportions required for producing metallic zinc, calcium sulphide and carbon monoxide. The fused calcium sulphide could then be tapped from the furnace and the sulphur subsequently recovered. All but traces of the zinc can be distilled from such a charge, as is shown by one of the experiments given above, in which the residue remaining in the furnace contained only 0.13 per cent. of zinc.

It is a question of only a few years until someone will devise an electric furnace process by which zinc ores, high in iron, etc., and which can not be treated by the old method can be economically smelted and by which practically all of the zinc in the ore will be saved.

The writers wish to thank Prof. C. F. Burgess for his helpful suggestions, and for placing at their disposal most excellent facilities for electric furnace experiments.

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University of Wisconsin.

DISCUSSION.

Prof. Burgess: The original idea of Mr. Brown when he undertook work on zinc reduction was that he could make calcium carbide and distil zinc simultaneously; this can undoubtedly be done, but the criticism of that plan from the practical standpoint would be similar to a criticism which might be offered in reference

to the Gin electric furnace process for producing steel, which was presented to us yesterday. To design a furnace to carry on two operations requiring different temperatures at the same time is next to impossible where economy and simplicity are considered. It violates a well-established principle in construction that a machine or furnace constructed to carry on one operation efficiently cannot attain other results essentially different at the same time, and maintain the efficiency.

Dr. Richards: I think it would have been much better if on page 177 there had been given more definite information than the mere statement that it simply took so much more current—so many more amperes—to do the work in one case than in the other. Mr. Johnson, in doing similar work, has given us the temperatures at which the reactions take place. In the reactions "A" and "B" the formation of carbon bisulphide is interesting, as it is a strongly endothermic compound and absorbs heat in its formation instead of giving out heat. The thermochemical equations furnish interesting discussion if analyzed.

In equation (a) for instance, there must be supplied:

To decompose 2 ZnS	86,000	calories
To decompose 2 CaO	263,000	"
To help form 2 CaC_2		
To help form CS_2		
Total absorbed	386,900	"
Furnished by 2 CO	58,320	"
Net heat absorbed	328,580	"

In addition to this immense amount of heat absorbed chemically, the hot products, if assumed to be at 1,300°, would contain approximately 150,000 calories of sensible heat, so that a total heat supply of over 475,000 calories must be supplied to the charge to distill off 2 Zn = 130 grammes of zinc, or over 475,000 large Calories per 130 kilograms of zinc.

Such a charge, in grammes, was worked off in an experimental laboratory furnace by a current of 50 amperes at 30 volts, for two hours. The heating value of this current is 2,500,000 gramme calories, showing a net efficiency of about 20 per cent.

On a large scale, 60 per cent. efficiency should be possible, at which rate 2 horse-power would produce 390 grammes of zinc in two hours, or at the rate of 5 horse-power hours per kilogramme of zinc, or 2.25 horse-power hours per pound. At 0.25 cent. per horse-power hour, the cost of power would be 0.56 cent. per pound of zinc produced.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 19, 1905, President Bancroft in the Chair.

CONTRIBUTION TO DISCUSSION OF BROWN AND OESTERLE'S PAPER.

(*Commercial Aspect of Zinc Smelting with regard to Progress of the Electric Smelting of Zinc Ore.*)

By Woolsey McA. Johnson.

It is pretty generally known in the zinc business that I directed a long series of experiments on the treatment of zinc ores in the electric furnace. There have even reached my ears in the East statements by outside people telling exactly how much money was spent in those experiments and exactly what results were attained. These reports were remarkable, both for their wonderful inaccuracy and the confident tone in which they were made.

It is, therefore, no breach of confidence on my part to make a few general remarks at this meeting on the commercial aspect of the subject. I hope this will stimulate to some degree discussions of the paper just read by Messrs. Brown and Oesterle. Direct and concrete statements are of course impossible.

First, let it be said that either of three things must happen in the zinc business in the course of the next ten years.

(1) Either the old retort furnace must be modified so as to treat with much less labor charges of low-grade zinc ores (from 30 to 35 per cent. Zn before roasting):

(2) Or there must be some great progress in ore-dressing so as to produce cheaply in this country a large tonnage of high-grade zinc ore (from 50 to 60 per cent. before roasting):

(3) Or there must be some radical change in the method of reducing zinc ore to metal, *e. g.*, the electric furnace.

It can be added to the enumeration that any combination of the above conditions for improvement will make a new complex treatment of zinc ores, which will be the successful treatment of the next decade.

The reasons for this are as plain as they are deep-seated, and

can be found in the underlying commercial conditions of the United States to-day.

For the past ten years the output of all useful metals has shown an average yearly increase in production and consumption of from 6 to 10 per cent. each year as fair values. The rate of 7 per cent. compounded for ten years means that the production doubles in ten years, and this has been in many cases exceeded. This figure of 7 per cent. is a conservative one, and in a measure determines the productiveness of capital, and thus, less some deductions, the normal rate of interest for money invested in the metal industry.

Now zinc is in a class by itself both commercially and metallurgically. Its use is indispensable in only a few industries, *e. g.*, brass-making, and any increase in price of spelter means that it is cheaper in construction work to use black sheets instead of galvanized sheets, and to replace these when rusted out. Thus the great market for spelter—galvanizing—is cut off automatically.

Metallurgically the extremely small size of the unit, (the retort holding from 40 to 60 pounds of ore on the average in this country, and each producing not over 7,000 pounds of metal each year,) brings it about that labor charge per ton of metal produced is extremely high. Thus there are in metal market and in plant rigid restraints to the increase in metal production of spelter, although in the past there has been an increase.

Labor, fire-clay and coal have all increased in price tremendously since 1896, and these are the largest factors in determining the cost of producing spelter from zinc ores. Perhaps 60 per cent. is none too high for this increase. The increase of smelting capacity in the last five years has brought about increase in selling price of ore. This is another bad factor.

The zinc smelter is thus between the upper and nether millstone. The demand for a high-grade ore is such that inordinately high prices are received for zinc ore, and the metal market is such that spelter cannot long sell for over $6 per 100 pounds for a yearly average. The result is coming that unless great progress is made, spelter production will not increase as it has done, or commensurately with the metals iron, lead and copper.

All these metals have been cheapened in cost of production by enlarging the capacity of furnaces and instituting labor-saving

devices. In these metals cost of treatment per ton raw material has been reduced, and thus it is possible to treat copper ores in the blast-furnace so low in copper content as to be regarded fifteen years ago as good "dump slag."

The metals, lead, copper and iron are all subjected to a primary reduction to metal or matte in a shaft furnace. Now the shaft furnace is susceptible of tremendous increase in capacity, and thus to large scale production. The zinc business is necessarily limited in the size of retort by the limitations of fire-clay.

There has been, it is quite true, great development in treating low-grade zinc ore from Leadville. Ores that were unsalable three years ago are now worth from $10 to $12 a ton in Leadville, and this price, an absurdly high one, is due to smelters bidding against each other. The proper way to treat a high iron-zinc ore is due to improvement in the metallurgy of the process. Losses that were once considered good would be considered poor work now. For instance, at the plant of which I was metallurgist, we reduced our average monthly losses per ton of ore 10 pounds of zinc a month for a considerable period. At the same time we increased our total monthly capacity 2 per cent. each month, and made considerable money out of our silver-bearing residues. All this was done in the face of an ever-increasing iron content in ores. Improvement similar to this has been made in nearly every plant in this country treating Western ores.

It is thus apparent that any radically new process has now a much tougher proposition to handle in the old retort than it had five years ago, and that if this improvement continues, it is possible that the difference might be so slight as to render the new process unnecessary.

There have also been great improvements in ore-dressing, due to careful classification and to the introduction of the electrostatic and magnetic separators, as well as the "flotation process" now being used at Broken Hill, Australia.

If this improvement continues, within a year there will be such a supply of high-grade ore as to put the zinc business in good shape and give any new process only a slight differential advantage.

There are also great possibilities in blast-furnace work on zinc ores either under pressure or by catching the metallic dust. The

attempts at leaching do not seem promising nor the "molten-bath chloride" decomposition by electrolysis. The expenditure of much energy and much money has produced by these processes very little metal, but only glowing reports. Unless the difficulties were great, so much effort would have produced results in the past ten years in these lines. Hall or Héroult did not take ten years to perfect the aluminum process.

Returning to the electric zinc furnace, it may be said that for treatment of ores it has undoubtedly possibilities. But there are very great difficulties incident to it. The furnace must be large to reduce radiation. It must be durable. It must make slabs of metal, not blue-powder. It must be designed not for the patent office, but for the works. All these characteristics can only be developed by large scale experimenting.

The only criterion of a successful process is actual large scale production.

However, the electric furnace can be used, and is used abroad for the production of high-grade metal from impure metal, and this at present is its legitimate sphere. This peculiar niche for metallurgical reactions is seen in the metallurgy of lead, nickel, copper and in the electric crucible steel furnace. In all these the electric furnace puts on the finishing touches.

The electric zinc furnace has the same advantages as the electric crucible steel furnace. (1) Large units in place of small units, with consequent decreased labor charge. (2) Ease of control over product. (3) Dispensing with costly fire-clay retorts and using instead a highly durable furnace with the heat inside where it is needed.

It is thus seen that the electric zinc furnace has its own peculiar field by the logic of the situation. In the wider field of reduction of ores, however, it has some strong—possibly too strong—competitors. Nevertheless, it is not impossible that it will win out, but it can only do so at the expense of great effort and large sums of money. If it had been an easy task, it would have been done years ago. But I can assure you that a large scale practical furnace, to beat the retort process in its present crude condition, not to say the retort increased in size, and combined with the introduction of machine chargers, etc., as is done in gas works, can only be built by overcoming many great obstacles, metallurgical, electrical and mechanical. This I know from practical experience.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 19, 1905, President Bancroft in the Chair.

NOTES ON THE ELECTROMETALLURGY OF ANTIMONY.

By Anson G. Betts.

The treatment of antimony ores, antimony sulphide and impure metallic antimony by fusion processes seems to be difficult and expensive, and the results not generally very good. As an illustration of this, there is a number of different makes of antimony on the market, with considerable differences in prices, which is in marked contrast to copper, for example, the metallurgy of which is so well known and understood. Commercial antimony often contains important quantities of gold. A chance sample which I assayed contained one and three-quarters ounces of gold per ton. Antimony ore quite often contains gold, so that the question of the purification of crude antimony should have some interest.

It has been proposed to use chloride solutions for the recovery of antimony from ores and from impure antimony, and to use alkaline sulphide solutions for the extraction of antimony from ores. (Processes of Koepp, Sanderson, Borchers, Siemens and Halske.)

Acid ferric chloride solution is said to attack stibnite with ease, producing a solution of ferrous and antimonious chlorides and a residue of sulphur, and from this solution metallic antimony and ferrous chloride should be recovered by electrolysis. I have applied the same idea to the treatment of crude antimony, and found that the electrolytic operation could be quite easily carried out. A diaphragm for the separation of the anode solution of ferric chloride and the cathode deposit of antimony would introduce difficulties, but it can be done without if the solution be allowed to remain quiescent during the electrolysis.

Carbon anodes and copper or lead cathodes may be used. The ferric chloride generated at the anode is heavier than the main solution, and continually runs down the anode surface and col-

lects at the bottom of the cell, whence it may be drawn off, while fresh ferrous chloride-antimonious chloride is added at the top.

My cell had a cathode area of 65 square inches and an anode area of 60 square inches; the height of the cathode was four inches and that of the anode seven and one-half inches. It is illustrated in the figures.

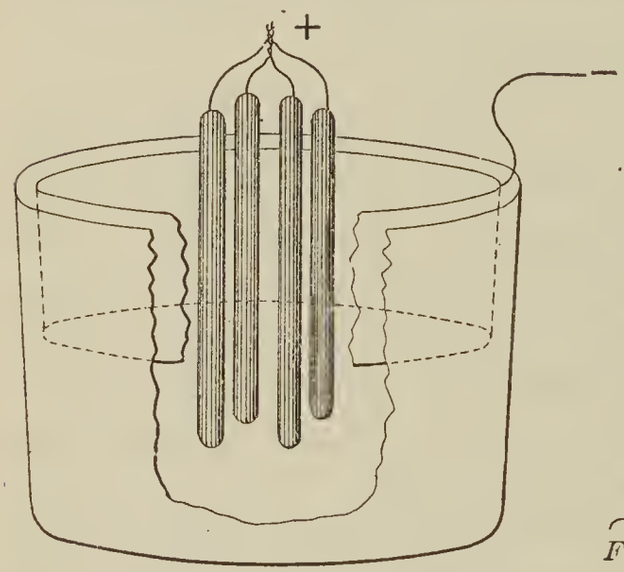


FIG. 1

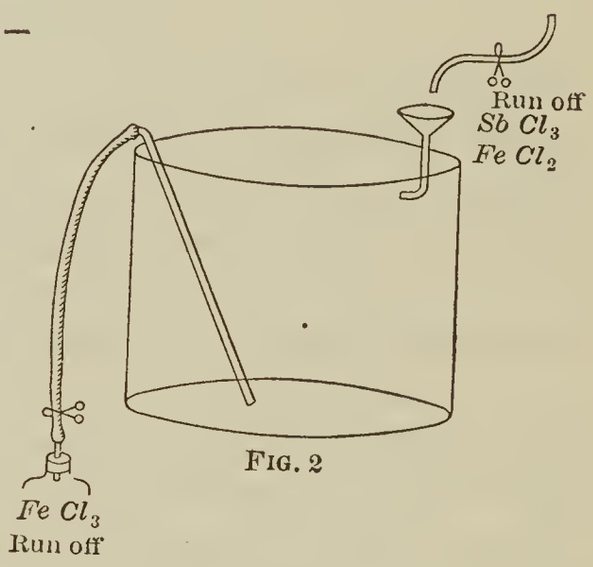


FIG. 2

The antimony deposit was hard and smooth, especially the lower portion, and on melting evolved considerable fumes. The current efficiency was 90 per cent.

TABLE I.

Time	Current	Voltage	Time	Current	Voltage
8.00 A.M.	4.2	1.10	12.00 M.	2.9	1.21
8.30 "	3.7	1.18	12.30 P.M.	3.1	1.23
9.00 "	3.4	1.23	1.30 "	3.5	1.23
9.30 "	3.2	1.27	2.00 "	3.2	1.25
10.00 "	3.0	1.32	2.30 "	3.1	1.27
10.30 "	2.9	1.32	3.00 "	3.5	1.21
11.30 "	2.8	1.32	3.30 "	3.5	1.21

Table I gives the result of one run of several similar ones. The antimony deposit was smooth and solid, though dark-colored. The current efficiency was 90 per cent. The electromotive force of the element $Sb\text{-}SbCl_3.FeCl_2\text{-}SbCl_3.FeCl_3\text{-}C$ is about 0.75 volt. The solution should be quite strongly acid to prevent the deposition of antimony oxychloride from the solution as a white precipitate.

Antimony trifluoride is much superior to antimony trichloride for electrochemical purposes. When a solution of it is electrolyzed with insoluble lead anodes, the main action at the anode is the liberation of oxygen as gas, and the formation of hydrofluoric acid in the solution, being thus similar to the behavior of a solution of copper sulphate when electrolyzed with a lead anode. When iron is present a good deal of ferric salt is formed, particularly with low anode current densities. A series of experiments gave the results given in Table II.

Antimony oxide is obtained in some metallurgical operations, such as the roasting of antimony sulphide, and this may be dissolved in hydrofluoric acid and electrodeposited from the solution with lead cathodes and lead anodes as a beautiful solid deposit,

TABLE II.

No.	Amperes per Square Foot of Anode.	Average Voltage.	Percentage of Current Used in Generating Oxygen Gas.	Solution.
1	87	3.4	75.3	7.5 gr. $Sb\,F_3$ } per
2	87	3.4	77.	5 gr. $H_2\,SO_4$ } 100
3	85	3.3	81.6	25 gr. $Fe\,SO_4$-7 $H_2\,O$ } cc.
4	86	3.3	82.4	
5	88	3.2	71.5	
6	81	3.2	72.7	
7	87	3.1	72.6	
8	85	3.3	71.4	15 gr. $Sb\,F_3$ } per
9	75	3.2	71.7	40 gr. $Fe\,SO_4$-7 $H_2\,O$ } 100
10	73	3.1	66.5	5 gr. $H_2\,SO_4$ } cc.
11	65	2.9	65.1	
12	45	2.6	52.	
13	31	2.7	42.5	

and, if the solution is free from copper and arsenic, of high purity.

Copper may be said to be the most troublesome metal in the electrometallurgy of antimony. In the chloride solution it stands very close to antimony in the electromotive force series, but in the fluoride solution it stands below antimony, and may be precipitated from solution by antimony. The explanation of this appears to be found in the fact that copper will exist in the fluoride solu-

tion only as a cupric ion, which has a different e. m. f. of solution from the cuprous ion of the chloride solution.

The electrolysis of ferrous fluoride-antimonious fluoride solution with a carbon anode, similarly to the electrolysis of the chloride solution, was not tried, for it did not seem that the substitution of a fluoride solution would be suitable in the treatment of an ore, on account of the action the fluoridion would have on the silica of the ore. It might succeed in the lixiviation of liquated antimony sulphide. Hydrofluoric acid solutions have the advantage over hydrochloric acid solutions, in that they permit the use of lead-lined tanks.

Electrolytic Refining and Plating of Antimony.

The chloride solution is not supposed to be suitable, and though first proposed a number of years ago, does not appear to have met with any success. When the fluoride solution was first tried alkaline sulphates and sulphuric acid were added to improve the conductivity, and in the hope of making the use of lead linings even more successful. Beautiful deposits were obtained, but if the anode contained even very small amounts of impurity the polarization rapidly increased, in some cases almost stopping the current entirely, and always causing the solution of impurities of the anode, such as copper, so that no purification was effected from copper.

In such a solution the current would be mainly carried by the sulphuric acid, and the anions liberated would be almost entirely sulphions, so that antimony sulphate would be primarily formed. Antimony sulphate would immediately decompose into basic sulphate, which would then have to be dissolved by the hydrofluoric acid present. If the anode contained lead, for example, there would be enough lead sulphate present to seriously interfere with the action of the hydrofluoric acid. It was therefore concluded that the cause of the trouble was the presence of sulphion, and experiment showed this to be a fact.

With the omission of sulphion there is no difficulty at all. The anodes dissolve as readily as copper or lead anodes and the cathode deposit of antimony leaves nothing to be desired. No analyses have as yet been made of the antimony, but there is no

reason to think that it is not very pure. These deposits do not tarnish at all, even in a laboratory full of fumes, when other metals tarnish badly, so that an electrolytic coating of antimony should be very useful as a protection against corrosion, especially on objects which are not bent, as the antimony coating is very brittle.

Troy, N. Y.

DISCUSSION.

President Bancroft: It certainly is very interesting to know that you can get a solution which will give a really satisfactory deposit of antimony; because in some cases one has a certain amount of trouble, and I take it, of course, that you had the same experience that Cohen had—that you do not get any explosive antimony in fluoride solutions.

Mr. Betts: I think that the explosive antimony may not be pure antimony, but a mixture of antimony and antimony pentachloride. When you heat this you get a reaction making antimony trichloride, and that supplies the heat which explodes the stuff.

President Bancroft: The last results of Cohen are that the explosion is due to the change of one allotropic modification to another.

Mr. Betts: I am familiar with that idea, but it seems to me that the other may hold, rather.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 20, 1905, President Bancroft in the Chair.

A STANDARD METHOD OF DETERMINING THE SPECIFIC RESISTANCE OF ELECTROLYTES.

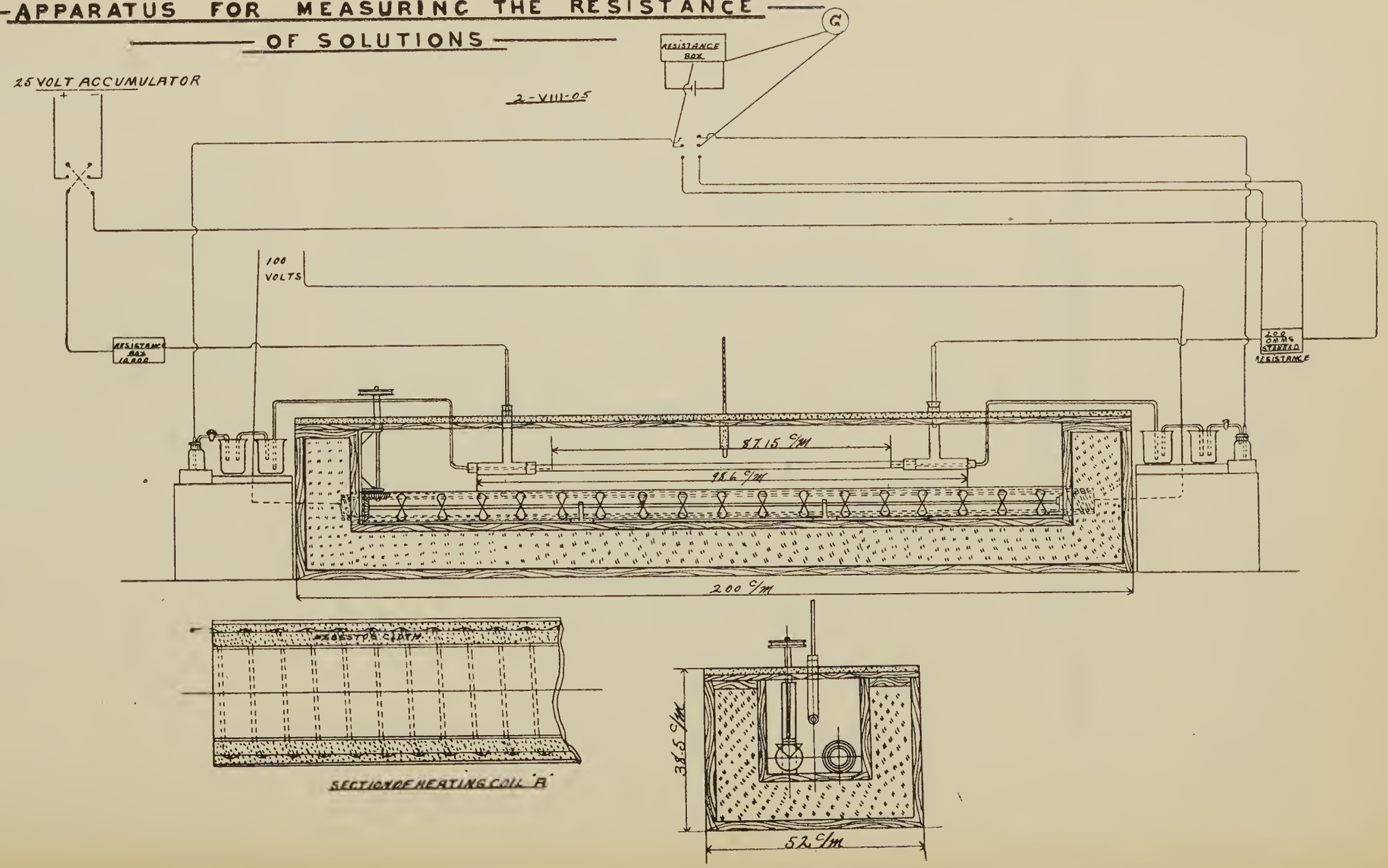
By R. Threlfall, F. R. S.

One of the earliest methods of measuring the specific resistance of an electrolyte is that of the potentiometer, or its electrostatic equivalent. The applicability of the method was, however, restricted by the difficulty of finding unpolarizable electrodes applicable to all solutions, and the experiments of Fuchs and Lippmann and Bouty, and more recently Hering, are the only ones I have come across in which the electrometer or potentiometer was employed. Recently an investigator has returned to this method and attempted to get over the polarizability of his metallic-testing electrodes by employing a high voltage.

It is not easy to believe that the obvious course of making use of single reversible electrodes, such as those of Ostwald, to connect the potentiometer to the electrolytic resistance has escaped attention, but so far as I have been able to ascertain this is actually the case. The experimental arrangements about to be described were set up in November, 1904, to meet a call for an accurate determination of the resistance of some solutions at different temperatures, and the method was selected merely on account of its being the most convenient with the appliances at hand, and without any idea that it was novel.

The experience gained has convinced me that no other method hitherto proposed affords so direct and accurate a means of comparing the specific resistance of an electrolyte with that of mercury as the method in question. My experiments having been made with a potentiometer the accuracy of whose coils was only guaranteed to two parts in 10,000, and which was not investigated by me, I am not able to claim to have made any absolute determinations worth communicating. I will merely say, therefore, that the results obtained with solutions of common salt agreed

APPARATUS FOR MEASURING THE RESISTANCE OF SOLUTIONS



with those of Kohlrausch within the error which a mistake of 0.1° C. in the temperature estimates would account for. The thermometers employed had been tested at Kew, and their zeros had been redetermined, but the scales were not very open, so that it was not possible to be certain of the standard mean temperature of the electrolyte to much less than 0.1° C.

In order to secure the best results of which the method is capable, it would, of course, be necessary to make some modifications in the apparatus used by me, which was intended to give results correct to about one part in 1,000, and was constructed with the idea of attaining this in the simplest manner and without much special manufacture of apparatus. The arrangement adopted will be clear from the drawing, which is to scale.

The essential part of the apparatus consists of a glass tube, 98.60 cms. long (to an accuracy of about $\frac{1}{10000}$) and a mean diameter of .9254 cms., as ascertained from two careful weighings of mercury to about the same order of accuracy, all at 0° C. The tube was slightly conical and was assumed to be so regularly—the difference of the end diameters amounting to about $\frac{1}{10}$ mm. The coefficient of thermal expansion of the glass was taken from Landolt & Börnstein, for glass of practically the same chemical composition. Two reference marks were made near the two ends of the tube by coating it with wax, and holding the edge of a sharp chisel against it as it revolved slowly on a lathe; the fine circular lines were etched by hydrofluoric acid and were found to be 87.155 cms. apart. This tube contained the electrolyte under investigation and fitted into two glass T pieces, one at each end, as shown. The vertical branches of the T's gave access to the platinized electrodes, while the horizontal branches were used to fix the position of the testing electrodes of glass tube drawn down to long fine points. The testing electrodes were merely held in position by rubber bungs strongly compressed, and were adjusted so that the free ends lay exactly in the same cross section as the reference rings. The testing electrodes were connected in the usual way through two beakers (containing respectively the solution under examination and the liquid used in the standard electrode) with the latter, which was of the Ostwald pattern, with a mercury surface of several square inches. By turning glass cocks the syphons could be put out of action and diffusion stopped. The

tube containing the electrolyte was immersed in a large bath containing heavy mineral oil and provided with a heating coil running the whole length, and a shaft with screw paddles also running the whole length of the trough. As comparison resistances, standards certified by the Reichsanstalt at Charlottenburg were employed and, of course, care was taken to have the resistance of the standards and electrolyte so adjusted that about the same voltage was operative over each part. It was found that the steadiest current was obtained when a considerable number of storage cells, 10 or 12, were in series with a large resistance—generally about 10,000 ohms.

It is an essential part of the method both that the main current be reversed after a group of observations and that several sets of comparisons be made alternately with the current, first in one direction and then in the other. The effect of taking an arithmetical mean of the results (if these are equally numerous with the current in both directions) is to eliminate differences of P.D. in the single electrodes and intermediate contacts, provided that these electrodes and contacts can be regarded as having a constant voltage. Since the currents passed through the electrodes during adjustment of the potentiometer are vanishingly small, the condition as to constancy is perfectly satisfied, and the comparison of potential differences is carried on with exactly the same ease as when metallic conductors are in question. The only inconvenience of any kind experienced was in relation to obtaining a steady current after reversal. The polarization of the platinum electrodes naturally assisted the current after a reversal, the effect falling off and the current with it for some time afterwards. It generally required about ten minutes for the reversed current to approximate sufficiently to its original value for a balance to be obtained, and during this time it occasionally happened that there was an appreciable change of temperature, which, of course, made it necessary to begin over again. The remedy no doubt would be found in providing two similar and symmetrically placed electrodes at each end of the tube of electrolyte and using them alternately according to the direction of the current, but I did not find the inconvenience above referred to sufficiently acute to induce me to make the change.

As an illustration merely I append a set of observations on the

specific resistance of an aqueous solution of sodium chloride containing 26.295 per cent. of salt by weight (this is a solution saturated at about 15° C.) at a mean temperature of 54.2° C.

The total voltage employed was about 25, and a wire resistance of 10,000 ohms was in series with the electrolytic resistance and the 200 ohms resistance standard.

Observations of Resistance of Solution of Sodium Chloride.

December 31, 1904.

Time.	Temperature by Standard Thermometer. No. 18371.	Tube.		200 Ohm Standard.		Resulting Resistance of Column of Electrolyte Ohms.	Current D.—Direct. R.—Reversed.
		Resistance in One Arm of Potentiometer.	Resistance in Other Arm.	Resistance in One Arm of Potentiometer.	Resistance in Other Arm.		
P. M.							
12 h. 10 m.	54.2	4000	1669	4000	1374	230.25	D
12 h. 20 m.	54.2	4000	1680	4000	1384	230.09	D
12 h. 25 m.	54.2	4000	1654	4000	1366	229.80	D
						Mean, 230.05	
12 h. 45 m.	54.2	4000	1678	4000	1369	231.75	R
12 h. 50 m.	54.2	4000	1679	4000	1370	231.70	R
12 h. 52 m.	54.2	4000	1681	4000	1371	231.80	R
						Mean, 231.75	
1 h. 10 m.	54.2	4000	1653	4000	1365	229.81	D
1 h. 15 m.	54.2	4000	1668	4000	1374	230.15	D
1 h. 18 m.	54.2	4000	1668	4000	1373	230.30	D
						Mean, 230.08	
1 h. 30 m.	54.2	4000	1684	4000	1373	231.82	R
1 h. 35 m.	54.2	4000	1684	4000	1375	231.58	R
1 h. 40 m.	54.2	4000	1683	4000	1374	231.60	R
						Mean, 231.66	

Grand Average 230.88

$$\text{Specific Resistance} = \begin{cases} \dfrac{\text{Measured resistance} \times \text{cross section}}{\text{Length between testing points.}} \\[2ex] \dfrac{230.88 \times .9254\ (1 + .000018 \times 54.2)}{87.155\ \ (1 + .000009 \times 54.2)} \\[2ex] 2.451 \text{ ohms per cubic centimeter.} \end{cases}$$

The errors inherent to the method and the conditions for securing the best result demand a brief reference.

1. The presence of the testing electrodes disturbs the stream lines and increases the apparent resistance. This necessitates the use of very fine capillary testing tubes for a length of about the tube diameter; also a column of electrolyte of considerable length in comparison with the diameter.

2. Heating of the column of electrolyte by the passage of the testing current. Owing to the low thermal conductivity of glass and the consequent impossibility of inferring the temperature of the electrolyte from that of the bath when heat is being generated at any appreciable rate in the former, it is necessary to use a very minute current. With a current of about $\frac{1}{500}$ ampère no inconvenience was experienced from progressive heating of the electrolyte, the heat generation being at the rate of 1.4×10^{-3} watts in the example given.

3. If any considerable current is allowed to flow through the liquid connections to the single electrodes, changes of concentration and alterations of P. D. will occur at the liquid boundaries. This, together with the high resistance of the testing terminals, makes it advisable to use a high resistance galvanometer. The instrument available in the experiment quoted was an ordinary commercial instrument of the moving coil type with a resistance of a few hundred ohms, and was far from being of ideal construction for the purpose. It was, however, amply sensitive enough for the potentiometer employed.

4. The reversal of the main current eliminates all inequalities in the P. D.'s of the single electrodes and connections, provided these are constant. It is much more convenient if the potentiometer is supplied with current for comparison from a large Clark cell,[1] as investigated by J. A. Pollock and myself. The constancy of such a current is much greater than of one drawn from an accumulator, and the adjustments of the potentiometer are correspondingly facilitated.

5. The adjustment of the capillary points within the main tube and the correct ascertainment of the distance between them is a matter of some difficulty if high accuracy is required and ordinary glass tube employed with the usual refraction errors. The deduc-

[1] "The Clark Cell as a Source of Small Constant Currents," Phil. Mag., *28*, 1889.

tion of the cross section of the tube by filling it with mercury is also a source of uncertainty unless the bore is very uniform, for the calibration of wide tubes is an uncertain operation. It is, therefore, better when standard determinations are in question to fill the tube and potentiometer connections with mercury and compare the P. D.'s as in the case of electrolytes; of course, with suitable modification of the potentiometer and resistance standard to meet the case of the increased conductivity.

6. The determination of the mean temperature of the electrolyte. The limit to the precision of the measurements is undoubtedly set by the difficulty of measuring the temperature. If a standard measurement is in question, no doubt the best way is to give up the advantages of a tube of geometrical shape and employ one with openings for thermometers at several points. If the simpler plan adopted in my experiments be employed, it is best to use a very small current and ascertain the temperature of the oil bath after the temperature has been steady for some time. A very active stirring of the oil is necessary in any case—more active than if water is employed in the bath. The advantage of oil, however, is that there is not so much risk of having conduction between the electrodes by leakage outside the tube.

In conclusion, I may perhaps venture to suggest that there does not seem to be any particular reason why mercury should remain the sole and universal liquid for resistance standards. By means of the balance it is possible to prepare solutions of very accurately known composition, and the method described above allows standard resistances of electrolytes to be compared with metallic resistances to a high degree of accuracy. For many practical purposes it is a question whether an experimenter armed with such an apparatus as I have described and taking advantage of Kohlrausch's observations on electrolytic resistance could not prepare resistance standards of any desired value with less trouble and as great an accuracy as is obtainable by testing and winding wire resistances.

The measurements referred to in this paper were carried out for me by my assistant, Mr. F. A. Stamps, who also constructed the greater part of the apparatus and made such modifications as were necessary to get it to work properly, and I have pleasure in acknowledging my indebtedness to him in the matter.

DISCUSSION.

Prof. Burgess: As compared with measurements on metallic conductors, our methods of measuring electrolyte resistances are difficult and inaccurate. The potentiometer method of measuring resistances is becoming more and more extensively used in measuring metallic conductivity, and its various advantages should make it the standard method where electrolytic conductors are concerned.

With the apparatus described by the author it is possible to obtain results which I believe can be depended upon more implicitly than can those attained by other methods. We have been employing a method similar to this as regular laboratory exercises for several years past in the Applied Electrochemistry laboratories of the University of Wisconsin. The apparatus which is employed differs in minor details with that described, and those differences present certain advantages.

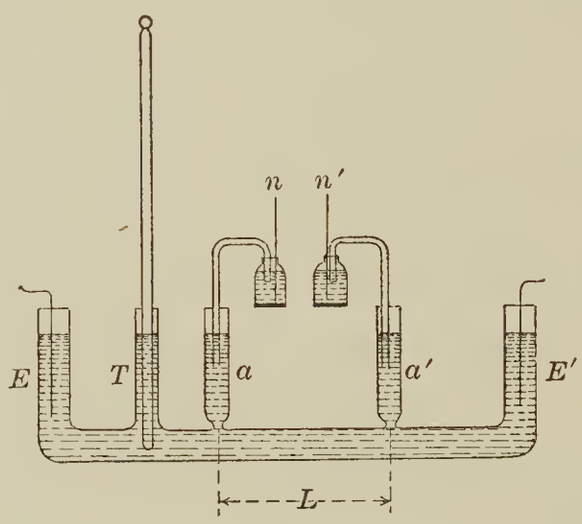


Fig. 1

Glass tubes of a form shown in Fig. 1 are employed. They have various lengths and cross-sections, depending upon the nature of the solution to be measured.

The branches a, á, which serve for the introduction of the normal electrode terminals communicate with the main tube through a small opening. The branches E, É serve for the current carrying electrodes, and the branch T allows the introduction of the thermometer bulb directly into the liquid being measured. By connecting the electrodes E, É, through a standard resistance

to the source of pressure, and comparing the fall of potential across a, a' with that across the known resistance of the resistance of the column of electrolyte L, can be derived. This can be converted into "specific resistance" by standardizing by mercury, or by use of a standard solution whose value is known.

This design is not perhaps capable of giving the highly accurate results which have been described in the paper just read, but it is convenient and enables determinations to be rapidly made. There is an advantage in having the thermometer directly in the liquid being measured rather than in the surrounding medium.

Might it not be suggested that the error which the author ascribes to the metal electrodes may be eliminated or reduced by the use of nonpolarizable electrodes of the Ostwald type. This would cause the current to attain a constant value at once, and enable the readings to be taken instantly upon closing the circuit and thus prevent heating and consequent change of the electrolyte.

Mr. Hering: I am very glad to see that some one is giving attention to this subject, because it has always seemed to me that the most desirable way to measure the conductivity of electrolytes, is with a direct current and not with an alternating current, as has generally been done heretofore. I therefore think Mr. Threlfall deserves much credit for working out this method with such success.

The method to which he refers as having been described by me,* was a rough and ready method which did not claim to be as accurate as the one which he uses. My idea then was to devise a method which can be used in the work shop with direct current Weston instruments.

There are several criticisms I would like to make of the author's apparatus. One is that there will be thermo-electric forces which may be appreciable in very accurate work. The thermo-electric forces are those in the beakers and other apparatus which are outside of the tank, and in the circuit in which no current should flow. I think he would get more accurate results if he placed these inside of the tank, so that they would all be at the same temperature. The thermoelectric forces at the two ends of that circuit, are ordinarily equal and opposite, and therefore tend to eliminate each other; but if there should be a difference in temper-

* Trans. Amer. Inst. Elec. Engineers; *19*, 317 (1902).

ature between the outside apparatus at these two ends, it seems to me it might affect the result, as the thermoelectric forces between solids and liquids appear, as a rule, to be considerably higher than those between two solids.

There will also be a contamination of the solutions at the main electrodes, at the tops of those T's. Here there will be electrolysis and the solutions will therefore be changed. In the case he cites, there will be sodium hydrate produced in one of them and chlorine gas in the other, and part of the latter will go into solution. This, I think, may explain the difficulty he had when he reversed the current, as he then has to undo with one current what the prior current did, before the normal conditions exist. To prevent contaminating that part of the liquid which is under test, these electrodes might be placed in porous cups.

I do not see why it would not be preferable to do what I suggested in my paper,—namely to use gold electrodes instead of the more complicated liquid connections and the Ostwald reversible electrodes. In my method I simply applied gold wires to the two points at which the potential was to be measured. I found they did not polarize like platinum or carbon, and gave very good results; but I did not carry it to the same degree of accuracy to which he carried it, and it may be that errors would arise in making accurate measurements.

Furthermore there may be precipitates formed in the little U tubes between those two beakers on each side. That depends, of course, on the solutions used; if the two solutions (namely, the solution used with the Ostwald electrodes, and the solution under test), are such as combine together to form precipitates, such precipitates will be formed in those two U tubes and may cause trouble. A method of avoiding such a contamination, and which I used many years ago in a Daniell cell, in the days when it was thought this cell might be made a standard, was to use a T tube instead of a U tube for connecting the two beakers. The third branch of the T was open to the air and permitted the mixed solutions to flow off as fast as they were formed. A little cotton wool or something similar was placed in the tubes to prevent the liquids from passing through too fast. The two different solutions will then never be contaminated by each other, because at the place where they mix they run off as fast or faster than they

can mix. There is another objection to using those inverted U tubes, which is, that bubbles of air are apt to collect in the upper part and they are rather hard to get rid of.

Mr. Easterbrooks: As high a degree of accuracy as is obtainable with this method is not necessary in the routine work of a metal refinery where quick volumetric methods are used for determining the composition of the electrolyte. An apparatus similar to that which Prof. Burgess has described, has its advantages in that it is simple in construction and a curve can be plotted in less than half an hour.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 20, 1905, President Bancroft in the Chair.

ELECTROCHEMISTRY IN 1904 AS REPRESENTED AT THE ST. LOUIS EXPOSITION.

[Complying with a suggestion made by Prof. W. E. Goldsborough, Chief of the Department of Electricity of the Louisiana Purchase Exposition, of 1904, this paper is presented to the American Electrochemical Society. It comprises a compilation of the notes made by Group Jury No. 68 (Electrochemistry) in connection with the study it made of the electrochemical and electrometallurgical exhibits at that Exposition.]

A large proportion of the more important electrochemical industries of this country were represented at the exposition, although in some cases the representation in question was unsatisfactory, frequently consisting of only a few samples of the products. It was noticeable that, almost without exception, the exhibits that were made represented substantial lines of scientific progress and commercial development, and few processes or products were shown that had not demonstrated their practical utility.

Inasmuch as the rapid advance which has been made in electrochemistry during the past two decades is to be attributed in large measure to the investigations and studies in electrochemical theories by German scientists, the exhibit made by Germany along this line was particularly interesting.

Work of German Electrochemists.

Germany's contribution to the exhibit consisted of a collection of apparatus and products sent by the Bunsen Society, and representing the researches of its leading members in the fields of physical chemistry and electrochemistry. The collection was of special interest in connection with a scientific study of electrochemical phenomena.

Dr. F. Kohlrausch contributed a number of pieces of apparatus made by himself, and including his well known cells for the determination of electrolytic resistance and the auxiliary devices for making measurements by the Kohlrausch method.

Dr. W. Ostwald, professor at Leipzig, was represented by his standard electrodes, electrometers, chemograph and other electrochemical apparatus well known to the physical-chemistry student. Mr. Fritz Koehler, of Leipsig, was a collaborator with Dr. Ostwald, the construction of the apparatus having been done by him.

Apparatus for the determination of dielectric constants, the normal hydrogen electrode, together with other electrochemical devices and a specially designed laboratory table, called attention to the work of Dr. W. Nernst, of Goettingen, Ruhstraat brothers and W. Apel, of Goettingen, executed the mechanical work, and George Bartels, mechanician at Goettingen, was also collaborator, being the maker of the electrometer of Nernst and Dolezalek.

Dr. Classen, of Aachen, contributed a model work-table for the conduct of electrolytic analytical work, embodying the most approved arrangement of switches, rheostats, electrodes, etc., such as he has described in his text-book on "Electrolytic Analysis."

Apparatus for measuring the mobility of ions was shown by Dr. R. Abegg, of Breslau, Erwin Kerker, of the same place, collaborating as its constructor.

A simple and ingenious device by Dr. Bredig, of Heidelberg, for measuring current by the observation of the height of a manometric column connected to a gas voltmeter, was shown. This instrument was called the ampère manometer, and was made by F. Hugerstorff, of Leipsig, as collaborator.

Dr. Coehn, of Goettingen, showed some interesting samples of metal which had been given thin coatings of carbon by an electrolytic process, which serves as a means for producing on polished metal surfaces a finish having various tints, such as brown, blue and dead black.

One of the most important exhibits in this section, judged from the standpoint of originality and scientific significance, was that made by Dr. P. Drude, of Giessen. It consisted of an apparatus for the rapid determination of the dielectric constants of conductive and non-conductive materials, the measurements being based upon the determination of the wave length of light passing through the material. The whole was a tribute to the ingenuity of the inventor.

The important work done by Dr. Karl Elbs, professor of organic and physical chemistry at the University of Giessen, was illustrated by a number of samples of organic and inorganic compounds, made by the electrolytic process.

An excellent exhibit of electric furnaces of various types was made by Dr. W. Borches, of Aachen. Some of these furnaces had an added historical interest, as they were the kind used by him in his pioneer work on high temperatures. Others, notably those for the production of calcium, embodied the most recent improvements in design. Almost all were of laboratory size, but one large enough for technical operation was also displayed.

The work of Dr. C. Harries, of Charlottenburg, was represented by an apparatus composed of ozonizing tubes of improved design, together with a high tension transformer for the production of ozone.

W. C. Heraeus exhibited various devices and materials which could be classed as electrochemical, but undoubtedly his most important achievement was shown in chemical apparatus from fused quartz. The electrical heating furnaces were of special interest. Their chief merit lay in the use of platinum resistances in the form of very thin platinum foil, instead of wire wound spirally around the refractory tube, thus enabling the attainment of a more intimate contact with the heater and the walls of the furnace to be heated, and making possible a high economy of platinum. An ingenious form of platinum electrode was also shown, the construction being such as to offer rigidity, combined with a large surface with a relatively small weight of the metal. This was accomplished by using thin sheet platinum, welded at frequent intervals to platinum wires passing through the walls of a glass tube, in the interior of which were conductors of a baser metal for distributing current to the various sections.

Much credit is due the makers of the various apparatus exhibited, special merit as regards mechanical construction and finish being justly earned by the Vereinigte Fabriken fuer Laboratoriumsbedarf, of Berlin, the manufacturer of many of the instruments shown.

Primary Batteries.

A large proportion of the electrochemical exhibits testified to the progress which has been made in, as well as to the present ad-

vanced state of the art of making batteries, both primary and secondary. The exhibitors showing primary batteries of the liquid type included the American Carbon and Battery Co., of St. Louis; the Batteries Supply Co., of Newark, N. J.; the Leclanché Battery Co., of New York; Leclanché & Co., of Paris, and the National Carbon Co., of Cleveland, Ohio. None of these exhibits showed any revolutionary improvements in battery construction, though demonstrating that progress has been made in the details of the mechanical construction and that greater attention is being given to the purity of the material employed.

One of the most interesting of the displays was that from the Leclanché Company, of Paris, which claims the honor of having originated what is known as the Leclanché type of cell. The exhibit included cells adapted to various classes of service, including telegraphy, telephony, induction coils, spark devices for gas engines and so on. The claims made for these cells include an absolute absence of all chemical action when the cell is standing on open circuit, the need of but little attention during constant operation, an economy of maintenance, absence of dangerous materials, such as acids, alkalies or salts of mercury, simplicity of electrolyte, and adaptability to transportation. The principal features of the Leclanche cell as shown are a cathode consisting of a mixture of conductive carbon and peroxide of manganese and an anode consisting of a sheet or rod of amalgamated zinc, the two electrodes dipping into a solution of sal ammoniac contained in a suitable vessel. According to claims made, the zinc suffers no corrosion when current is not flowing, and the peroxide of manganese, being completely insoluble, produces no chemical action on open circuit.

No radical difference in the principal features of construction was shown in the Leclanché type of cells manufactured by other companies.

The closed circuit type of cell was illustrated by the well-known Edison-Lalande battery, shown in the exhibit of the Edison Battery Co., and in the Gladstone-Lalande batteries in the exhibit of the Batteries Supply Co., of New York. The improvements to which the last-named exhibitors called special attention consisted of a mechanical method for removing and replacing the copper oxide plates as they become exhausted. The negative

plate, of agglomerated oxide of copper, is suspended in a supporter frame or hanger of copper and is held in position by two perforated flat spring clamps bearing on the flat surface of the plate, one of them being riveted to the support of the hanger and the other detached, so as to allow the copper oxide plate, when exhausted, to be readily removed. As in other Lelande cells the positive electrode is of a pure grade of zinc alloyed with mercury, the electrolyte being a 20 per cent. solution of caustic potash protected by a layer of pure mineral oil.

The greatest development in primary battery manufacture was shown in the "dry cell," which in the last decade has been so greatly improved that it is apparently replacing the liquid cell. Proof of this lies in the enormous number now being annually produced by the various companies which made exhibits, an estimate of the value of their total product showing that this phase of manufacture has become an electrical industry, ranking with those industries which measure the value of their product by millions of dollars annually.

The size of cell most extensively manufactured is 6 inches long and 2½ inches in diameter, cylindrical in shape. The earlier dry cells, as is well known, were most unsatisfactory because of their small capacity and their rapid deterioration when not in use. A great deal of study has been put upon the matter by the various manufacturers, and their attempts to overcome the defects of the earlier cells have met with much success. The improvements which have been effected have resulted in a lower internal resistance, a longer life on open circuits, or, as the trade designates it, a better "shelf wear," a greater number of ampère hours per unit of weight and immunity from explosion and similar accidents. The tendency formerly prevalent among manufacturers of attempting to make the public believe that each had a mysterious and secret formula for making his particular battery superior to all others, is gradually disappearing. The claims which are now made are for an approximate perfection approached not so much through the use of new materials or by reason of novel features of construction as by the employment of materials having the highest degree of purity, put together in such manner and in such proportions as to give the best possible satisfaction. It is claimed that the purest grade of zinc which it is possible to

obtain is used in the manufacture of these cells, and it is undoubtedly due to this fact that the low depreciation on open circuit is secured.

The capacity of such cells is determined by the length of time which they will operate and the number of ampère hours which they will deliver, and this, in turn, depends largely upon whether the cell is used continuously or intermittently. The end of the dry cell's life is determined when the electrolyte is completely changed from ammonium chloride to zinc chloride, or when the zinc becomes consumed, or the depolarizing material is exhausted, or when the internal resistance increases to a high value, which may be due to the consumption of the electrolyte or to the evaporation or leaking of the liquid. This last may be caused by the seal being broken, or the zinc, constituting at once the outer electrode and the containing vessel, becoming perforated. It appears to be a common practice among manufacturers to choose the least factor in determining the life of the cell. In other words, the materials are so proportioned that the zinc gives out first, by becoming perforated.

Although the six-inch cell is the most common size manufactured, various other sizes are made, these being adapted to different kinds of service. In the exhibit of the National Carbon Co. was what was probably the largest dry cell ever manufactured, it being several feet high and capable of delivering over 1,000 ampères. It is needless to say that it was more of a curiosity than a regular article of commerce.

While it is recognized that the manufacture of a dry cell larger than the standard size and having all of its properties is an easy matter, it has not been demonstrated until recently that a very small cell can be made, comparable in capacity per unit weight and durability to the larger sizes. During the past few years much attention has been given to the manufacture of a small dry cell, and marked progress has been made as shown by the exhibits. Cells having dimensions of approximately three inches in length by seven-eighths inch in diameter are used for lighting the miniature lamps which are most extensively employed as novelties, although devices of a more practical nature have thus been made possible. The pocket flash lamp furnishes a market for the greater number of these small cells, and the output of the

various factories along this line has reached a really amazing figure. These cells have an electromotive force of about 1.4 volts, and the normal amount of current which they deliver on intermittent service is about .2 of an ampère. The makers of these cells state that their construction has been made possible by the use of materials of the highest degree of purity obtainable. Those who exhibited cells of the sort included the American Electric Novelty and Mfg. Co., of New York; the Electric Contract Co., of New York; the Howard Electric Novelty Co., of New York, and the National Carbon Co., of Cleveland, Ohio.

The exhibit of the National Carbon Co., of Cleveland, Ohio, included samples of various sizes and types of cells, both wet and dry, illustrating the most advanced stage of primary battery manufacture. The company, it appears, furnishes the carbon for the greater proportion of batteries now being manufactured in this country. A great variety of forms of electrodes were shown by it, in addition to complete cells of both the liquid and dry type. A new type of dry cell recently developed is a closed cell intended for service such as that for which the Lalande cell is adapted, and constructed on somewhat analogous lines.

The Wesco Supply Co., of St. Louis, in connection with a number of electrical appliances, exhibited some dry cells, which had, however, no special features distinguishing them from those of other makes.

In the exhibit of the Western Electric Co. were found a number of dry cells of the standard six-inch size, but no information either as to their special characteristics or the magnitude of the business, represented by them was given by the exhibitors.

The Leclanché Battery Co., of New York, had on display a large number of their standard type of liquid open circuit cells. The principal foreign exhibitors of primary cells were the Leclanché Company, P. Delafon, of France, and Hellesens, Enke & V. Ludvigsen, of Denmark. The two companies last named manufacture dry cells which differ from the American type in the more general adoption of the rectangular form in preference to the cylindrical, most common in this country. The Delafon cells were shown in a number of sizes, such as are adapted to bell installations, telegraph and telephone service, electrotherapeutic appliances, electric measuring, signals, etc. The

special claims made for this cell related to its adaptability for work through a wide range of temperatures. The company offers to repair or renew worn-out cells at a charge of 90 per cent. of the purchase price.

The characteristics claimed as a special feature of the Hellesen dry cell are long life and the possibility of withstanding lengthy storage without loss of electromotive force. It is this type of cells which the German Government employs for its official telephone sets throughout the German post-office district, purchasing over 100,000 annually. The company also states that the Swedish Government has adopted the cell for its postal service. The rectangular-shaped cells have electrodes of a similar shape and have, consequently, a greater capacity per unit of volume than is obtainable by the use of round electrodes, while they are, at the same time, more durable. It appears that this company manufactures over 500,000 of these cells annually, sending them out all over Europe, our high tariff being, apparently, the reason for not placing them on sale in this country.

Storage Batteries.

The firms exhibiting storage batteries or accumulators included the Dayton Electric Mfg. Co., of Dayton, Ohio.; the Edison Storage Battery Co., of Orange, N. J.; the Electric Storage Battery Co., of Philadelphia; Henri Fredet, of Isere, France; the Gould Storage Battery Co., of New York; Société Chelin, Limited, of Brussels.; Société Gramme, of Paris. The only working batteries in which the cells were shown complete were those displayed by the four American concerns.

The display made by the Electric Storage Battery Co. constituted the most extensive and complete working exhibit of storage batteries in the exposition. The main part consisted of large-size accumulators of the station type, connected to regulating and charging equipment, such as is installed for central station working. The latest type of stationary accumulator recommended by this concern consists of the well-known Manchester positive, with a new form of negative which has been recently developed. This is known as the "box" negative, in which the active material is held in place by windows in the cast grid by means of a per-

forated lead screen which is welded to the grid after the material to be transformed into a spongy lead has been inserted. The claims made for this type of plate are that the depreciation is greatly reduced and the capabilities of withstanding high rates of charge and discharge are increased. Another feature of this cell worthy of notice lies in the use of wooden sheet separators, the wood being previously subjected to such chemical treatment that it neither deteriorates nor exerts a harmful action on the electrolyte.

Other types of cells especially designed for various kinds of service, such as train lighting, were shown, together with the well-known Exide cell for automobile service. The exhibit as a whole represented the most advanced stage reached in the manufacture of storage batteries, although nothing radically new in the construction of lead cells was revealed.

The exhibit of Gould cells, by the Gould Storage Battery Co., of New York, represented the highest development reached in the manufacture of a cell by the Planté method of formation. The distinguishing feature of this type of cell was that its mode of manufacture makes it possible to use chemically pure rolled lead for the plates, the greater disintegration attendant upon the use of alloys being thus prevented. The extensive lead surface is attained by a special "spinning" process owned by the company, by which leaves of the desired thickness and depth are obtained. After the plates have thus been given suitable surface, the active material is formed by an electrochemical process. The capacity per pound of plate is determined by the amount of active surface, and it is, therefore, possible to adjust the capacity by regulating the thickness, depth and spacing of the leaves. This fact is taken advantage of in the adjustment of the positive and negative plates, so that they will have equal capacities, a difference in the active surfaces of the two making this possible. One of the marked characteristics of this type of construction is the extremely high rate of charge and discharge which the cell can withstand, this being due to the large amount of active surface and the intimate contact of the active material, which also conduces to low internal resistance and to high efficiency.

The cells shown were of various types designed for various kinds of service, such as for central stations, car lighting and

automobile work. The portable cell known under the trade designation as the "E. P. battery" consists of a positive of pure lead which has been given a large surface by the Gould "spinning" process and is then electrochemically formed. The negative plate is of the pasted type. The separator used is of hard perforated rubber sheets placed against the surface of the plates, with the spacing ribs which prevent short-circuit and allow space for the electrolyte.

The accumulators of the Dayton Storage Battery Co. were designed principally for use in connection with the sparking devices for igniters, the principal distinguishing feature being that the two containing vessels are cast together as one mechanical unit, of lead alloy cast under pressure, forming two compartments separated by a metal partition. Into each of these compartments a lead electrode is placed, a positive in one and a negative in the other. The interior walls of the lead containing vessel constitute the positive electrode for one side of the cell and the negative for the other, so that one mechanical unit is electrically equivalent to two storage cells in series, giving a voltage of over four volts. The advantages claimed for this style of construction are economy in dispensing with the rubber containing vessels, durability and the avoidance of half of the terminal connections, the construction being such as to avoid buckling, leakage of electrolyte and disintegration of plates. This type of cell presented nothing radically new in accumulator construction.

The Edison Storage Battery Co. had a working exhibit of the new Edison nickel-iron cell. An interesting portion of the display was that which was given up to samples of plates, "pockets" and active materials, showing the historical development of the cell in recent years. The Edison storage battery is designed almost exclusively for automobile and other portable service and its principles of construction and operation are so well known that a description is scarcely necessary. The present status of this type of cell has been best stated in a paper read before the International Electrical Congress at St. Louis by A. E. Kennelly and S. E. Whiting.

It appears that the cell has been developed to such a point as to be successful for certain classes of service, though that it has not yet reached its ultimate degree of perfection is to be

inferred from the fact that radical improvements have been made upon it recently. The cell known as the type D was first completed in May, 1903, and consisted of 28 plates (14 positive and 14 negative), giving a capacity of about ten watt hours per pound of complete cell. It was found, however, that these plates were not equally balanced as regards their capacities, and this led to the development of the type E cell, which embodies the latest improvements, and which was shown in the working exhibit. This cell is made in three sizes, known as E-18, E-27 and E-45, respectively. In this type of cell there are twice as many nickel plates as there are iron ones, thus giving equal capacities in their positive and negative electrodes, and giving a slightly higher capacity per pound than was attained in the older form of cell.

This exhibit was remarkable, as it demonstrated the possibility of constructing a practical accumulator from materials other than lead, and a cell capable of withstanding the roughest treatments as to rates of charge and discharge, standing discharged on open circuit, and mechanical shocks. A great amount of ingenuity was shown in the mechanical construction of the cell, such as the welding of the case, the coating of the same with a durable coating of nickel and the devices by which evaporation, leakage or the carbonation of the electrolyte were prevented, while the gases had free escape, thus avoiding the possibility of explosion. So far as durability, ability to withstand rough treatment and, perhaps, capacity per unit of weight is concerned, this battery represents a distinct advance in portable accumulator construction, though as regards electrical efficiency in power and low initial cost it can not compete with a well constructed cell of the lead type. The excess of the charging voltage over the discharging voltage is much greater than in the lead type of cells.

The following data, taken from A. E. Kennelly's paper, to which reference was made before, may be given for the latest type of cells:

Type.	Positive plates.	Negative plates.	Capacity in ampere-hours.		Normal charging current.	Normal charging time.	Weight complete.		Dimensions over all (excluding trays).							
									Length.		Breadth.		Height.		Volume.	
			Nor.	Max.	Amp.	Hours.	Lbs.	Kilos.	Ins.	Cms.	Ins.	Cms.	Ins.	Cms.	Cu.ms.	Cu.cm.
E-18	12	6	110	140	40	3.75+	12.5	5.66	5.1	13.0	2.6	6.6	13.2	33.5	175	2,874
E-27	18	9	165	210	60	3.75+	17.5	7.95	5.1	13.0	....	....	13.2	33.5	.....	.....
E-45	30	15	275	350	100	3.75+	30.0	13.6	5.1	13.0	....	....	13.2	33.5	.....	.....

The exhibit of Henri Fredet, of Isere, France, showed plates in various stages of construction, with grids, pastes, etc., but none of the cells was set up complete with electrolyte. This style of accumulator is new, having been manufactured only since 1901, and it showed some improvements over other types, its chief claims being a reduction in initial cost and an increased durability and strength. The cell is intended chiefly for use in central station work. Both plates are of the pasted type, the advantages claimed being attained by the use of ammonium hydrosulphide in connection with the oxides of lead with which the grids are pasted. The use of this material, it is claimed, causes an increase in the density of the active material and a remarkable degree of cohesion between the plate and the active material. It is claimed, also, to preserve the negative from sulphating, thus allowing an increase of acidity in the solution without detriment to the plate. The Societé Gramme, of Paris, showed in connection with an extensive exhibit along other lines an accumulator of the pasted type, though it was not complete with electrolyte. No information as to special merits or distinguishing features was given out.

The Societé Chelin, of Brussels, exhibited parts of a small accumulator enclosed in a celluloid case, claims for great capacity per unit of weight being made. The cell exhibited simply showed the supporting grids, but without active material or electrolyte.

Electrochemical Products.

The exhibits dealing with the application of electricity to the manufacture of chemical products includes those of the Acker

Process Co., Niagara Falls; Castner Electrolytic Alkali Co., Niagara Falls; Niagara Electrochemical Co., Niagara Falls; the Union Carbide Co., of Niagara Falls; Solvay & Co., of Brussels, and the United Alkali Co., of Great Britain. None of these exhibits consisted of more than a display of the products manufactured.

The exhibit of the Acker Company consisted of bottles of caustic soda and bleaching powder, made by the electrolysis of fused sodium chloride, and also samples of tetrachloride of tin, oxide of tin and tetrachloride of carbon manufactured by using the chlorine liberated in that process. This company, which was incorporated in 1899, has developed an industry of magnitude, the process used being that developed by Charles E. Acker and his collaborators, and known as the Acker process.

The Castner Electrolytic Alkali Co. exhibited bottles of caustic soda and bleaching powder made by the well-known Castner process. The sodium hydroxide produced is claimed to have a purity of over 99.5 per cent., while the content of bleach in available chlorine was placed at 38 to 40 per cent. The other qualities of bleach to which attention was called were its desirable physical properties, including its fine white color, powdery nature, freedom from grit and lumps, solubility and rapidity of settling, and its ability to give a clear bleaching liquor.

The Niagara Electrochemical Co.'s exhibit consisted of samples of metallic sodium and peroxide of sodium. The first named is manufactured by the electrolysis of fused sodium hydroxide, and is, in turn, converted into peroxide.

The United Alkali Co., of Great Britain, which had a large exhibit in the Manufacturers' Building, displayed there samples of potassium and sodium chlorates, chloride of lime and caustic soda made by electrolytic methods.

The exhibit of the Union Carbide Co. represented the products of the factories it operates at Niagara Falls and Sault Ste. Marie, and consisted of packages of calcium carbide, together with the crude materials from which the carbide is made.

Electrothermic Products.

The exhibits relating particularly to the electrothermic appliances and processes, including the Union Carbide Co.'s exhibit,

which has been referred to previously, were those made by the Carborundum Company, International Acheson Graphite Co., Norton Emery Wheel Co., Pittsburg Reduction Co., and the Siloxicon Company.

One of the new electric furnace products exhibited for the first time was alundum, made by the Norton Emery Wheel Co., of Worcester, Mass. This material is a crystalline oxide of aluminum, made by melting the mineral bauxite. While it has been long known that crystallized aluminum oxide could be obtained by electric fusion, it is only recently that a method for doing so on an industrial scale has been worked out. The inventor of the process is Mr. Charles B. Jacobs, the methods of operation and the details of furnace construction having been developed by Mr. A. C. Higgins, manager of the company's works at Niagara Falls. Alundum may be considered an artificial carborundum, but it has decided advantages over the natural material for use as an abrasive on account of its purity, toughness of crystals and other properties, making it specially advantageous for use in the manufacture of grinding wheels. This company was represented by three exhibits, one in the Palace of Mines and Metallurgy, where a section of an electric furnace, samples of aluminum oxide in its raw and its manufactured form, and a large amount of fused materials were displayed; another in the Palace of Electricity showed an internal section of the electric furnace, while the third, in the Palace of Machinery, consisted of a good-sized exhibit of carborundum and alundum wheels, showing the forms in which the material is now placed on the market.

The Carborundum Company, of Niagara Falls, had a model of the electric furnace used in the manufacture of carborundum. In this a cross section of the furnace was exposed, and different grades of materials, varying from the large crystals to the fine amorphous and undecomposed materials, were shown. Beautiful specimens of carborundum crystals were on display in the Palace of Machinery, where the abrasive value of the material was demonstrated. Samples of siloxicon and metallic silicon, manufactured in a furnace similar to that used in the making of carborundum, were also shown. Several hundred pounds of metallic silicon, made in the furnace designed by Mr. F. J. Tone, formed

an interesting portion of this exhibit, particularly when viewed in the light of recent progress. Until recently this material has been classified as a chemical curiosity, and price lists gave it a value of several hundred dollars a pound. Now Mr. Tone has demonstrated the possibility of producing it in large quantities and at low cost, and the problem at present is to find suitable and extensive uses for it. The company quotes a price of 35 cents a pound, and so far its best utilitarian application has been in the production of copper and copper alloys and certain grades of steel.

Observation and study of the operation of the carborundum furnace have led to the discovery of a compound of oxygen, silicon and carbon in certain proportions, and to this compound, previously unknown, the name "siloxicon" has been given. The materials from which it is made are the same as those used in the manufacture of carborundum, and its production depends upon a suitable regulation of the energy delivered to the furnace. This material has been found to be exceedingly refractory, resistant to the action of acid and basic slags, non-fusible, insoluble in molten metal and, in a measure, self-binding. These characteristics make it very valuable in various lines of metallurgical work. Uses which have been found for it include its employment in the manufacture of permanent molds for casting metal, as a foundry facing, and the making of refactory crucibles and furnace linings. So important has it come to be regarded that a concern known as the Siloxicon Company has been incorporated solely for the purpose of making and handling the product. Both this company and the Carborundum Company exhibited samples of the compound.

The International Acheson Graphite Co., of Niagara Falls, presented in its exhibit, which was on display in the Electricity Building, small models of the type of electric furnace in which artificial graphite is made and in which carbon articles are graphitized. The exhibit also showed the various grades of graphite which are produced, and a large number of electrodes for electrolytic and furnace work. Another exhibit in the Palace of Mines and Metallurgy included similar samples of graphite products. The process by which they were made is too well known to require description here. It is owing to the inventions

of Mr. E. G. Acheson that the company is able to duplicate by art nature's process for producing graphite. The distinguishing characteristics claimed for graphite made from carbon are great purity, uniformity, high electrical conductivity, lubricating properties and chemical inertness to oxidation and disintegration. This industry, while being an important electrochemical one in itself, has been found to be of great assistance in promoting industrial electrochemical development by furnishing for electrode purposes a material of such excellence that the success of several electrochemical industries may be said to depend thereon.

The carbons from which the graphitized electrodes are made are furnished to the International Graphite Co. by the National Carbon Co., which has co-operated in the manufacture of the useful product handled by the former concern.

Carbon Electrodes.

The exhibit of the National Carbon Co., while of interest to the electrochemist from the battery standpoint, also has an importance in connection with electric furnace developments. As stated previously, the Acheson Graphite electrodes are made from carbon furnished by this company. There are many furnaces and electrolytic operations in which the decreased deterioration of the graphitized carbon is not sufficient to warrant the increased first cost, and for this reason there is a large market for the ungraphitized carbon supplied by the National Carbon Co. Special attention has been given by this concern to the composition, manufacturing and making of the material, that the most durable electrodes may be obtained, and much improvement in quality has been achieved during recent years as a consequence of this.

Other exhibitors showing carbons for electrolysis and furnace work were the Compagnie Française des Electrodes of Lyons, France, and the Società Italiana Dell' Electrocarbonium of Rome. The first named company showed various sizes of electrodes up to those having a dimension of 40 cm. by 40 cm. and 150 cm. long. The specific resistance of this material is given as between 4.5 and 4 ohms per cubic centimeter. It is made of petroleum coke, carbon or anthracite, in accordance with the requirements to be met. The company claims an output reaching 4,000 tons a

year, the product being consumed by the various graphite, electrochemical and electrometallurgical factories in the Alps. The Italian exhibit of carbon, while not so large as the French display, proved the ability of the company to manufacture large-sized electrodes of a high quality. This company has an output exceeding 1,000 tons a year, all consumed by the electrometallurgical industries.

Aluminum Exhibits.

The exhibit in the Metal Pavilion of the Pittsburg Reduction Co. demonstrated the many and various industrial uses to which aluminum has been put. While no data were furnished by the company that might indicate the magnitude which the aluminum business has reached, the exhibit spoke for itself through the medium of the many articles displayed. They included automobile frames, automobile parts, covers and parts of electrical instruments, electrical feeders, bus bars and connections, cooking utensils, tableware, typewriter parts and many novelties. Alloys of various degrees of hardness and with properties making them adaptable to certain distinct uses were also shown. It is of interest to note that the exhibit did not prove that electroplating upon aluminum has become an established process. It may be that this is due to the fact that aluminum requires no ornamentation nor protection coating, but it is more probable that as yet no satisfactory method of applying the coating has been worked out. While the exhibit itself could not be considered as a direct electrochemical display, it was of special interest to the electrometallurgist, as it showed the remarkable results which have been achieved by the use of a metal produced exclusively by electrolytic reduction.

Another exhibit having to do with the production of aluminum was that made by the Société Electrometallurgique Française, which, while not entered among the electrochemical exhibits, was of special interest. This company was organized in 1888 for the manufacture of aluminum and other processes by the Héroult process, and it has grown to be one of the largest producers of aluminum in the world. Quantities of its products were shown in the exhibit made by the company in the Palace of Mines and Metallurgy, including besides aluminum, ferrochrome, ferro-

silicon and other iron alloys. A model of the Héroult oscillating electric furnace for the treatment of steel electrothermally was also on display.

Other Furnace Products.

In the British section of the Palace of Mines and Metallurgy were shown samples of the products of the Electric Reduction Co., of Buckingham, Quebec. These consisted of about 400 pounds of ferrochrome, made in the electric furnace from the chromite of Black Lake, about 75 pounds of ferrosilicon, made from silicate, and phosphide of iron from apatite.

New Water Purifier.

The Electra Water Purifier Co., of St. Louis, had an interesting working exhibit consisting of an electrolyzing apparatus in which water can be sterilized, settling tanks for clarification and filters. It is claimed that 99.98 per cent. of organism in the water is destroyed by this process, mainly through oxidation by electrolytically generated oxygen. The most striking feature of the apparatus, aside from its improved methods of construction, lay in the use of a special aluminum alloy as the anode material, this being of such a nature that the anode was but slightly corroded. The apparatus on exhibit had a capacity of from 50 to 500 gallons per hour, depending upon the quality of the water treated. The cost of purification is estimated at one cent per 100 gallons. The normal rate at which energy is consumed in the practical operation of the process was put at 1 watt hour per gallon.

Electrodeposition of Metals.

The industries based upon the deposition of metals from aqueous solutions were represented by various exhibits, which did not, however, do full justice to the magnitude which these industries have reached. The electrolytic deposition of metals is carried on chiefly for the protection or ornamentation of other metals and for the refining and purification of metals and their recovery from their compounds.

The Hall Gold and Silver Plating Co., of Chicago, operated a small electroplating plant, the equipment of which consisted of

small tanks for gold, silver and copper plating, polishing and buffing wheels and a small motor generator. Emphasis was laid on the deposition of non-conducting surfaces, and a variety of articles were shown (and offered for sale), including such as leaves, twigs, fruits, etc., which had been plated with gold, silver and nickel. While such novelties testified to skill and ingenuity, they did not present anything new in the line of electrodeposition. One claim made by the exhibitor was to the effect that by improvements in the electrolytes for gold plating he is able to obtain polished depositions of gold of considerable thickness in a few seconds. His performance seemed to bear out this assertion, but like most practical platers he preferred to withhold information concerning the composition of his solutions, only admitting that they were cyanide baths. Similarly, it was stated that inasmuch as the method of plating upon non-conducting surfaces was discovered by the exhibitor only after "years of patient investigation," it was not deemed advisable to reveal the details.

Sherard Cowper—Coles & Co., Ltd., of London, had an interesting exhibit in the British section, in which were displayed samples of various kinds of metal deposition, models of tanks for the production of copper tubes and sheets and for the rotation of electrodes. There were also samples illustrating the new non-electrical process of applying zinc coating, which has come to be known as "sherardizing."

Throughout the world this company is known for its work upon cold processes of galvanizing. Processes which they have extensively installed in various European countries employ acidified zinc sulphate solutions, lead anodes, and a circulating device by which the electrolyte is drawn from the depositing tank and regenerated by passing through another tank containing finely divided metallic zinc, usually in the form of zinc dust. The samples showed that zinc coatings deposited by this means have a remarkable adherence, being able to withstand bending and distortion of articles to which they have been applied.

A more remarkable process, at least from the standpoint of novelty, is "sherardizing," which, according to recent publications in the *Electrochemist and Metallurgist*, consists of the following salient features: The articles, whether of iron, brass, aluminum, or almost any other metal, are placed in an iron

cylinder partially filled with zinc dust, in which they are imbedded. Air is exhausted from the cylinder, and after it is subjected to a temperature that is several hundred degrees below the melting point of zinc for several hours the zinc forms a coating upon the surface. It is said that this coating possesses great adherence and durability, as it actually alloys with the underlying metal. Samples of brass rods, aluminum and other metals which had been subjected to this process appeared to bear out the claims made for the coating.

This company also makes a specialty of rapid deposition of copper for the production of tubes and sheets. Their process has been described in a general way in the technical press, and the possibility of using current at as high as 200 ampères per square foot, while producing a coating of great density and toughness, is made possible by a rotation of the cathode. To this centrifugal action is claimed to be due the excellent qualities of the ensuing deposition. Samples of copper sheet thus produced showed considerable density and toughness, and the crystalline appearance usually so noticeable in electrically deposited metals was scarcely discernible.

An interesting division of the exhibit was that dealing with the production of parabolic reflectors for searchlights. The method for producing these is described in detail in the *Electrochemist and Metallurgist* for March and April, 1901, and need not be repeated here.

Other exhibits dealing with metal deposition were found in the Mines and Metallurgy Building. In the exhibit of the International Nickel Co., various samples of electrolytic nickel were shown, but these possessed mostly an historical interest only, as they demonstrated the various attempts which have been made to refine this metal electrolytically. A large nickel cathode, about 3 x 2 feet and ¼ inch thick, made by the old Balbach electrolytic refining process, was shown, as were also eight nickel cathodes weighing about 25 pounds each and made by the Browne electrolytic process. These cathodes, although over an inch thick, showed by their porosity, roughness and crystalline nature something of the difficulties encountered in depositing this metal to any considerable depth.

In the Robert Means Thompson historical exhibit were dis-

played a number of pieces of electrolytically deposited nickel, made in experiments conducted by the Orford Copper Co.

Of interest to electroplaters were the anodes of nickel sent by the Hanson & Van Winkle Co., the Zucker, Levett & Loeb Co., and C. Upham Ely. The Hanson & Van Winkle anodes of the latest and most approved type had an elliptical cross-section, by reason of which an even corrosion is attained, together with a large amount of active surface, a minimum amount of scrap being produced. The Zucker, Levett & Loeb anodes were of the corrugated type, the grooves running vertically.

In the Japanese section the Osaka Electric Refinery exhibited large copper cathodes and quantities of gold and silver recovered in the electrolytic process of silver refining. Samples of electrolytic copper from the plant of Fujita & Co. were also shown.

In the Educational Building, among other exhibits from the University of Wisconsin, was shown a piece of electrolytically refined iron, weighing 30 pounds. It was the work of Prof. Charles F. Burgess and Mr. Carl Hambuechen, and is probably the largest piece of electrolytic iron which has been produced so far.

Conclusions.

The remarkable progress which during recent years has been made along electrochemical lines, the phenomenal results attained in the use of electric energy as an agent in producing chemical and physical transformations, and the improvements which have been effected in the generation and storage of electrical energy by chemical means, might have justified the expectation that the electrochemical exhibits at the exposition would have formed a striking feature of the whole. This, however, did not prove to be the case. The spectacular was little in evidence and even educationally the exhibits were disappointing. It may be said that electrochemical products were well represented, though in most cases they were included in exhibits of other products in such a way that no special attention was called to the fact that electricity had been used in their manufacture. Little information was offered to the public, however, regarding methods and processes, and but few working exhibits were made.

Perhaps this fact may be taken as indicative of the substantial

growth and the firm position which electrochemical methods have attained. It is, perhaps, more illustrative of still another fact, that most electrochemical concerns consider their success in the commercial field largely due to their ability to keep to themselves their knowledge and their methods, and it is largely to this that the difficulty of securing exhibits of the desired kind may be ascribed. Whether or not this policy of secrecy is justifiable is not to be discussed here, but it is undoubtedly true that as the electrochemical industries increase in number and importance more liberal views will be adopted and that at future expositions electrochemistry will occupy the position which it justly deserves.

Great credit is due to Prof. W. E. Goldsborough, the Chief of the Department of Electricity, for his earnest efforts in securing electrochemical exhibits for this exposition, notwithstanding the difficulties due to the desire of many of the manufacturers to preserve strict secrecy concerning their products.

The members of the International Jury of Awards on Electrochemistry were as follows: Carl Hering (United States), chairman; Dr. Kahle (Germany), vice-chairman; Prof. Charles F. Burgess (United States), secretary; Dr. Samuel Sheldon (United States), K. Gosnowski (France).

CHARLES F. BURGESS, *Secretary.*

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 20, 1905, President Bancroft in the Chair.

REVERSIBLE AND IRREVERSIBLE ELECTROLYTIC POLARIZATION.

By W. S. Franklin and L. A. Freudenberger.

(*Second Paper.*)

The method used in our previous work[1] for the determination of the irreversible polarization of a Cu—$CuSO_4$—Cu cell was to find the total electromotive force, E (= Ri + f (i) + e), across the cell at the instant of starting the current, so that the reversible polarization *e* due to changes of concentration of the electrolyte, changes of temperature, and changes in the electrodes would be zero, whence, knowing the value of Ri, we would have the value of the irreversible polarization f(i).

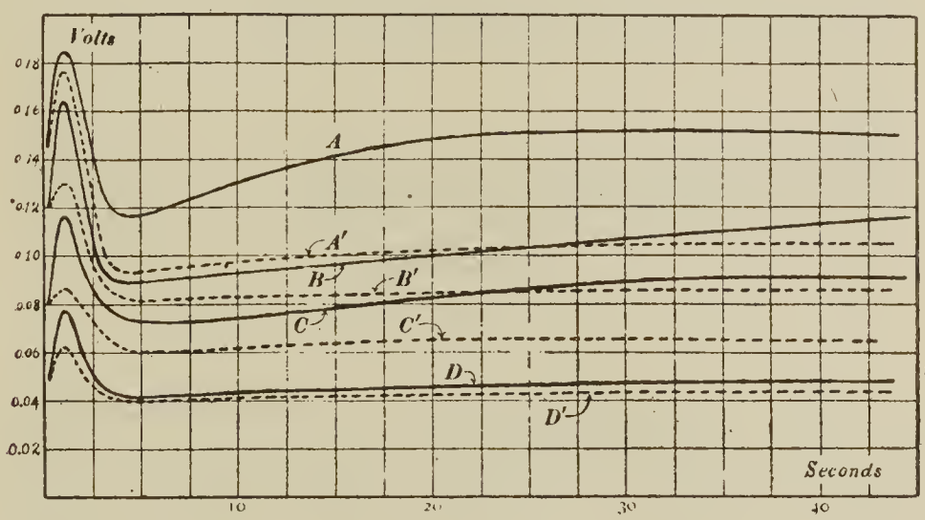


Fig. 1

In order to find the value of Ri + f(i) + e at the instant of starting the current, the curve of growth of total voltage across the cell with time was determined with the expectation of exterpolating to zero time.

Figure 1 shows the complete set of voltage-time curves obtained by us. The ordinates of these curves represent the values

[1] Trans. Amer. Electrochem. Soc., 7, 33 (1905).

of E—Ri(= f(i) + e), and the abscissas represent time elapsed after closing the circuit.

Curve A, current 1.5 ampères flowing up.
Curve A′, current 1.5 ampères flowing down.
Curve B, current 1.0 ampère flowing up.
Curve B′, current 1.0 ampère flowing down.
Curve C, current 0.5 ampère flowing up.
Curve C′, current 0.5 ampère flowing down.
Curve D, current 0.25 ampère flowing up.
Curve D′, current 0.25 ampère flowing down.

The electrolytic cell consisted of a vertical glass cylinder with two horizontal disks of copper as electrodes. Sp. gr. of solution

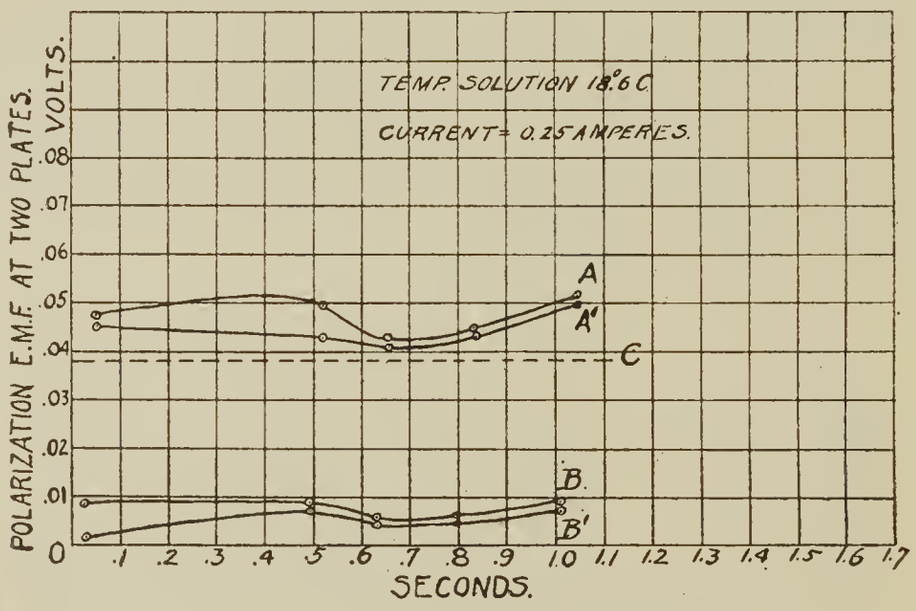


FIG. 2

of $CuSO_4$ was 1.160 at 18.5° C., sp. resistance 15.24 ohms per cubic centimeter at 18° C., area of each electrode 96.05 square centimeters, and distance between electrodes was 0.626 centimeter. The temperature of the cell was approximately 18° C. in each case. The slight variations of temperature and the slight deviations of current values from those above specified have no important bearing upon the results.

The sudden rise of voltage immediately after the closing of the circuit, which shows itself in all of the curves of Fig. 1, makes it impossible to extend the curves to zero time with accuracy, so that the values of the irreversible polarization obtained from the curves of Fig. 1 are unreliable.

During the spring of 1905, Mr. L. F. Blume and Mr. S. H. Fleming, working under the direction of one of the authors, carried out a series of measurements so arranged as to give the

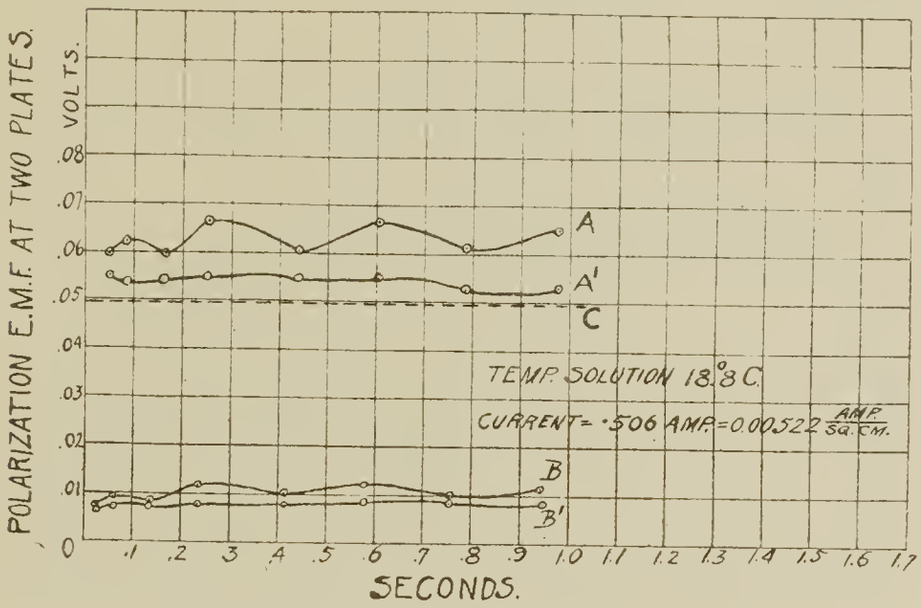


FIG. 3

values of the reversible polarization e with considerable accuracy, thus enabling the values of the irreversible polarization, f(i),

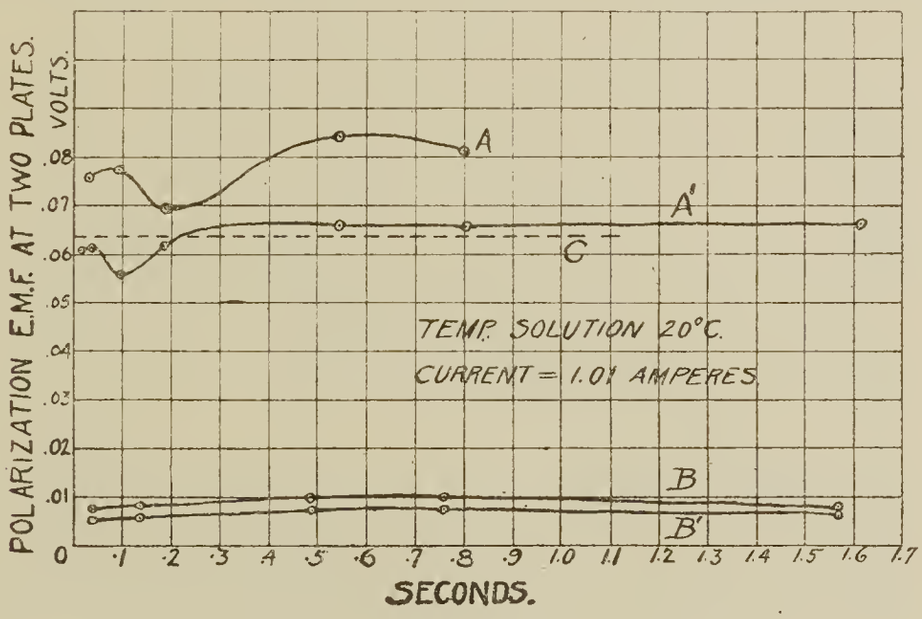


FIG. 4

to be inferred with considerable accuracy from the measured values of Ri + f(i) + e.

The electrolytic cell used by Messrs. Blume and Fleming was the same as that used by the authors as described in their Boston

paper,* the electrodes being horizontal copper disks in a vertical cylindrical vessel of glass. The area of each electrode was 96.05 square centimeters, and the distance between the electrodes was 0.626 centimeter. The copper sulphate solution used by Messrs.

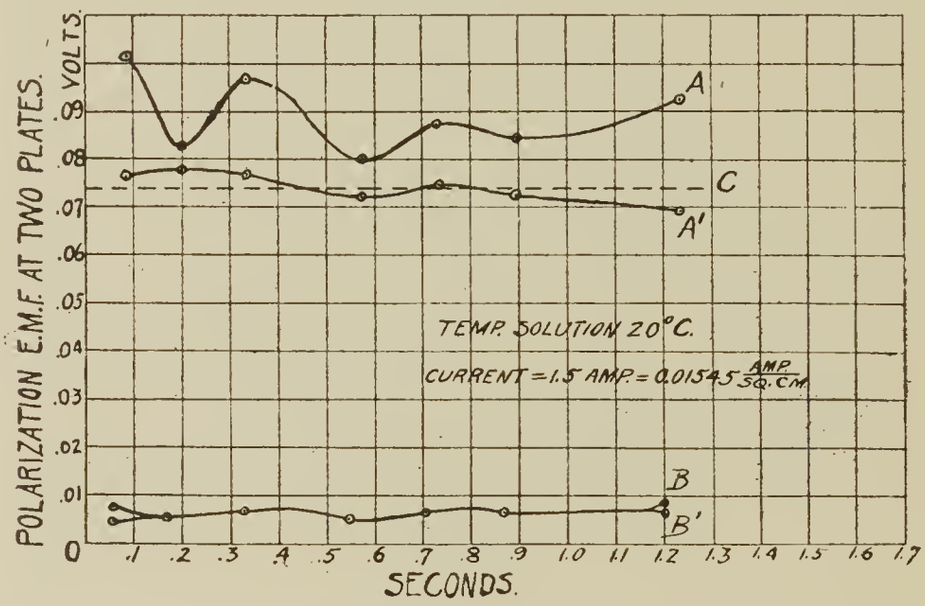


FIG. 5

Blume and Fleming had a specific gravity of 1.146 at 18.8° C., and it was acidulated with ½ per cent. of H_2SO_4. Messrs.

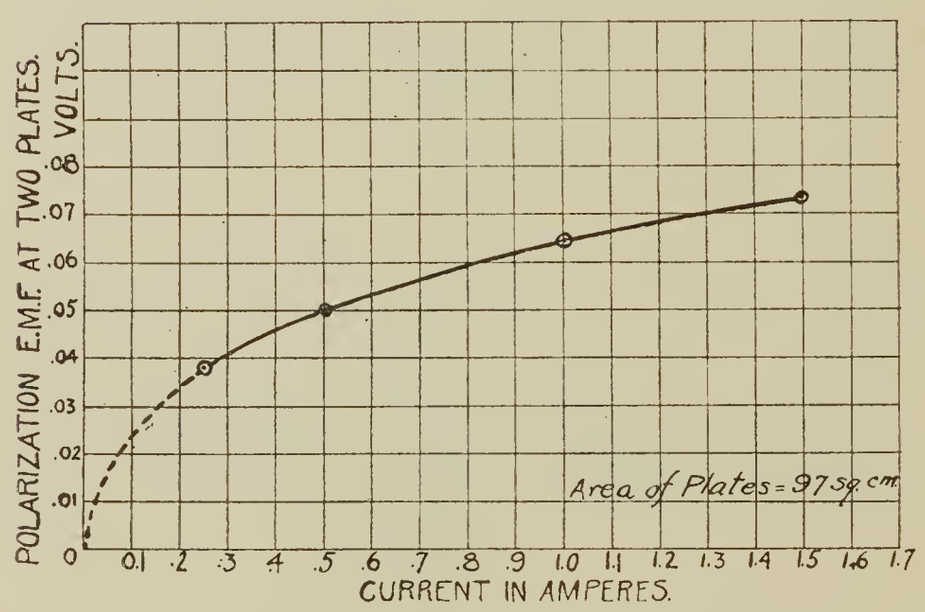


FIG. 6

Blume and Fleming used an instantaneous contact method for measing voltage across the cell, using for this purpose the dash-

* Loc. Cit.

pot apparatus that was used previously by the authors, modified slightly so as to enable the voltage to be measured, not only *t* seconds after the circuit was closed, but also immediately after the circuit was broken after being closed for *t* seconds. Complete details of the apparatus and of the method of procedure is given in the manuscript thesis of Messrs. Blume and Fleming, which is deposited in the Electrical Engineering Library of Lehigh University.

The following is an outline of procedure sufficient to make the results of Messrs. Blume and Fleming intelligible: A certain value of current was started through the electrolytic cell and allowed to flow for *t* seconds, when the voltage between the cell terminals was measured. From the voltages so determined the calculated value of Ri is substracted and the result is plotted as an ordinate of the A and A′ curves in Figs. 2, 3, 4 and 5, the abscissa being the value of *t*. The electrolyte was then vigorously stirred, the same value of current again started through the cell and allowed to flow for the same length of time, when the circuit is suddenly broken and the residual voltage between the cell terminals immediately measured. This residual voltage is assumed to be the value of the reversible polarization *e* at the instant *t*, and this residual voltage is plotted as an ordinate of the B and B′ curves in Figs. 2, 3, 4 and 5. The elapsed time between the breaking of the circuit and the measuring of the residual voltage was about 0.01 second.

Thus the ordinates of the A and A′ curves in Figs. 1, 3, 4 and 5 represent the values of E—Ri ($= f(i) + e$), and the ordinates of the B and B′ curves represent the values of *e*.

A and B refer to up-flowing current and A′ and B′ to down-flowing current.

The regular undulations of the A and A′ curves are presumably due to slight variations of *e*, which accompany the systematic régime of current reversals between successive runs, and these variations show themselves in the corresponding undulations of the B and B′ curves.

The smaller amplitude of the undulations in the B and B′ curves may be due in part to a decay in the value of *e* during the short interval of time between the breaking of the circuit and the measurement of the residual voltage, and in part to the

fact that each point on a B or B′ curve is determined immediately after the corresponding point on an A or A′ curve, so that when a point on the B or B′ curves is determined a greater time has elapsed since the reversal of the current just preceding the determination of a point on the A and A′ curves. Assuming the undulations to be due to slow changes in the electrodes following a reversal of current, the amplitude of the undulations of the B and B′ curves should, under these conditions, be smaller than the amplitude of the undulations of the A and A′ curves.

It seems that the best that can be done to find the values of the irreversible polarization from the observations represented in Figs. 2, 3, 4 and 5 is to take the mean difference of the ordinates of the A and A′ curves on the one hand and the ordinates of the B and B′ curves on the other hand. These mean values of f(i) are shown by the ordinates of the straight lines C in Figs. 2, 3, 4 and 5, and these mean values of the irreversible polarization f(i) are plotted as a function of the current in Fig 6.

South Bethlehem, Pa.

DISCUSSION.

Prof. Burgess: Would it be possible to make measurements in using an alternating current?

Prof. Franklin: I don't believe it would. The fundamental idea is the distinction between that part of the polarization electromotive force which is a function of the current, and that part which is not a function of the current. That part which is a function of the current, of course, would be periodic and very difficult to measure if you used an alternating current; on the other hand, that part which is not a function of the current, would, I imagine, be zero in the case of the alternating current. The question concerning the irreversible electromotive force is as to what kind of a function of the current it is, and it would be very difficult from an observed distortion of the electromotive force wave to work backwards, analyze that distortion and derive from it the desired function. In the case of copper sulphate and copper electrodes, the irreversible polarization (see Fig. 6) seems

to be a square root function of the current, and it would be very difficult to derive that function from alternating current measurements.

PROF. BURGESS: The humps of the curves given on the first page are ascribed to a polarization as a function of the current. It seems to me that there is another phenomenon that exerts an influence. I have described this in a paper presented at the last meeting, and I am a believer in it, although it does not seem to be in very good standing. This is the "transfer resistance"—a resistance which is right at the surface of the electrode. This transfer resistance is always present when an electrode makes contact with an electrolyte, and is, to a certain extent, a function of the current flowing. As the current passes, the film resistance, or whatever it is, changes. I have in my notes, somewhere, a curve of a shape similar to those given, and taken between two copper electrodes in a copper sulphate solution, in which the hump goes up to 20 or 30 volts, instead of one or two volts; then drops off. This is produced under certain circumstances when high current densities are used. Just what conditions serve to increase or decrease this effect I am unable to give, but expect to make further observations thereon.

MR. CARL HERING: I have already discussed the first paper of these authors, and as it is in print, I will not repeat it here. I cannot quite agree with the authors that the relations are so beautifully simple as they have contended in their fundamental mathematical equation. Mathematically, of course, it is very simple and unquestionably correct to mass together all the heterogeneous parts which make up the whole, and then divide them into two groups, and say that what is not in one group must be in the other. But is such a beautifully simple mathematical process applicable to this case of the division of the e. m. f.'s? May there not be some e. m. f.'s in the circuit, which are not a function of I, nor belong to the group *e*. If so, then there is no term in that equation which includes them. Unless I am very much mistaken the thermo-electric E. M.F's are of this kind, and there is nothing in that equation which would include them. When there are so many different factors, as there are in this case, I think it is dangerous to separate them into only two groups as has been done here. I hardly think it is correct to do so, although I may be mis-

taken. For instance, in the very apparatus which they used, it seems to me that there is a factor which enters into that equation and which has not been duly considered. The authors used *horizontal* copper plates. Now we know very well (and I have had occasion to say it before this Society several times), that when a current is passed in the upward direction, a layer of uncolored liquid will form under the cathode; it is sulphuric acid, all the blue copper sulphate having been reduced. That layer is, in the first instance, only molecular and not visible; but it soon becomes visible, and can be seen with the naked eye. The original conditions of the experiment then no longer exist; instead of two copper electrodes in copper sulphate there will now be a copper cathode in the sulphuric acid, and a copper anode in the sulphate of copper. This undoubtedly occurred in their test, unless they stirred the solution very rapidly. When the current passes in the opposite direction (down) this will not happen, and the two electrodes will both continue to be in sulphate of copper. Now in their tests they subtracted the voltage in the one case from that in the other. But is not this a little like subtracting a number representing oranges from a number representing apples? Mathematically you will get a result, but what does it mean? They are subtracting voltages obtained when both electrodes were in the sulphate, from those when one was in sulphuric acid, and therefore not at all under the same conditions.

There is another element which enters, and which does not appear to be included in their equation. It is this: if a current is passed in an upward direction between two horizontal copper plates in sulphate of copper, the current is actually lifting copper from the anode to the cathode; it is performing pure mechanical work, lifting copper against gravity. The work for doing this must appear somewhere; it appears in the voltage; it must take a higher electromotive force to send the current in the upward direction, than in the downward direction; in the downward direction the copper is lowered from the anode to the cathode, hence the voltage required will be smaller. This unquestionably occurred in their tests, but whether the difference was appreciable or not, I could not say. It would be a very simple matter to calculate what this difference would be; but in any event it is one of the factors which make up the E, and should therefore be included in their general equation.

PRESIDENT BANCROFT: It seems to me that in any case of electrolysis you have at least two changes taking place: a possible change in the state of the electrode and a certain change in the concentration of the solution. Unless there is very vigorous stirring both those factors come in; and it seems to me, that so far as I understand the paper it would have been very satisfactory if this work had been supplemented by measurements made when the stirring was as intensive as could possibly be obtained so as to see what differences occurred in those two cases.

MR. HERING: May I ask why horizontal electrodes were used? Why not use vertical electrodes and thereby get rid of both the effects that I called attention to? It seems to me to be very dangerous to use horizontal electrodes in such tests.

PROF. FRANKLIN: In regard to the point that Professor Burgess spoke of, I must say that I think he has made an important suggestion. In working out the theory, and planning out the experimental work, I have had in mind the things connected with the actual deposition of the ions. In so far as those processes are concerned which actually enter into electrolysis, I think the formulation that I have given of the two parts of the electromotive force cannot be questioned. On the other hand, a film on the electrode might offer a genuine resistance to the flow of current, and not be concerned with the irreversible generation of heat by the falling of the ions onto the electrodes. I think that such a film would really introduce complications which would vitiate the results of our first paper. I think the change of current would have to be made in so short a time that the variation during that time of the film resistance would be negligible; and, furthermore, that the film would have to be assumed to follow Joule's law—or to conform to Ohm's law.

Irreversible polarization is not intended to mean film resistance, it is intended only to have to do with the generation of heat at the electrode on account of the irreversible deposition of the ions out of a super-saturated solution, or the going of the ions into a solution which is under-saturated. I personally feel very much obliged to Professor Burgess for calling my attention to this film resistance. I have, as a matter of fact, overlooked that particular aspect of the electromotive force losses at the electrodes, in thinking too specifically of the ionic processes or

what I conceive to be the ionic processes, which constitute electrolysis.

Now in regard to thermoelectromotive forces, I think Mr. Hering means that they are functions of temperature.

MR. HERING: They are, of course, a function of the temperature also; but what I meant to emphasize was that they would *not* belong to those which are the function of i.

PROF. FRANKLIN: They would come under reversible electromotive forces. In order to judge whether the various component parts of the total electromotive force of polarization which Mr. Hering mentions are taken account of in our paper, it is only necessary to consider what parts do not disappear when the current is reduced to zero in zero time, and what parts do disappear.

The reversible polarization of an electrolytic cell depends upon the "free energy" of the reaction which accompanies the flow of current. This free energy depends upon the character of the surface layers of metal on the electrode, upon the concentration of the electrolyte in immediate contact with the electrode, and upon the temperature. All these are material conditions, and they cannot change with mathematical quickness when the current is changed to zero.

On the other hand those parts of the polarization electromotive force (if they exist) which are dependent upon the *process* of electrolysis itself, cease to exist when the process ceases. Thus the falling down of the ions upon an electrode out of a supersaturated layer would involve an irreversible electromotive force which would cease to exist when the current ceases.

In regard to the use of vertical in preference to horizontal electrodes, it does not seem to me that there is any choice whatever between the two, in view of the fact that the theory takes complete account of electromotive forces due to concentration changes and to temperature effects, and of the E. M. F.'s associated with the chemical changes in the electrodes.

I am very much obliged to Professor Burgess for what he has said in regard to film resistance. It is curious how a point like that will escape one's mind.

MR. S. S. SADTLER: Have you any idea how much it would influence the curves?

PROFESSOR FRANKLIN: Film resistance when properly consid-

ered, should have no influence upon the results of our method. Film resistance may very likely have to do with those humps in the electromotive force curves when the current is started, but the sudden stopping of the current, it seems to me, would not give time for those resistance films to be developed; so that the experimental work which is represented in this second paper seems to me to be free from any ambiguity.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 20, 1905, President Bancroft in the Chair.

AMMETERS FOR ELECTROLYTIC WORK.

By Lawrence Addicks.

In very few branches of industry does the cost of power form so large a proportion to the total cost as in certain kinds of electrolytic work. Therefore, in such work the energy efficiency of the process must be carefully followed, and every endeavor should be made to keep the switchboard instruments correct to one per cent.

With voltmeters there is little trouble, though the same precautions must be taken with regard to the effect of stray field as stated below for ammeters. The very heavy currents met with in electrolytic work accentuate some causes of error which are ordinarily negligible in switchboard ammeters, and if one per cent. is to be attained, distribution of the current in the shunt, thermoelectric effects, switchboard temperature, magnetic effect of stray field on the instrument and possible dynamo action of the leads, must be accounted for. One per cent. may be taken as the limit of accuracy of the best types of switchboard ammeters for heavy direct currents.

When several thousand ampères are to be measured, care should be taken to place both shunt and instrument in suitable positions when designing the switchboard. In the first place the shunt should be obtained from the maker with short bars inserted in the slots usually provided in the shunt terminals, these bars in turn to be bolted to the bus bar carrying the current to be measured. In this way the shunt is calibrated with the same distribution of current through the various leaves, as will be the case in after use. It is practically impossible to disconnect a high capacity shunt down to the slotted terminals and put it back in place again without altering the calibration more or less, due to change in the distribution of the contact resistance between main bar and shunt terminals, and consequent slight change in the amount of

current carried by the different leaves of alloy. This, in turn, slightly affects the ratio between drop of potential between binding posts and total current carried. These changes in resistance are very small, but the total resistance of a good 5,000 ampère shunt is but about 0.00001 ohm. There is no way to detect the error introduced in this way except by calibration *in situ.*

Unequal heating of the two shunt terminals will introduce a constant error from the thermo-electric junctions formed where the alloy leaves are soldered on to the copper blocks. This may easily amount to one per cent. of the full scale reading, may be either positive or negative, and will show as a zero error on shutting down the circuit which will gradually disappear as the shunt cools off. Sometimes compensating devices are applied to avoid thermoelectric errors, but if the shunt is so placed in the bus bar that the facilities for conducting away heat are approximately equal on both sides, there will be no appreciable error, and such devices should be unnecessary. The alloy leaves of a shunt would be red-hot at full load were it not for the heat dissipating qualities of the large copper terminals. There should be practically equal radiating surfaces of bus bar for three or four feet each side of the shunt. If placed close to a switch on one side, there is sure to be a thermo-electric error in the shunt, as high capacity switches frequently run hot. The best plan is not to attempt to place the shunt back of the switchboard at all.

The temperature at which a shunt runs will depend upon how heavily it is loaded and the opportunity afforded to dissipate the heat generated. The temperature indicated by a thermometer and well placed upon one of the terminal blocks should not be allowed to exceed 200° F., owing to the danger of starting the solder and consequent failure. The temperature coefficient of the alloy used in the resistance leaves is generally so low that no correction to the instrument reading need be applied for the heating of the shunt.

The power wasted by a 5,000 ampère shunt at full load is about 300 watts. It is perfectly practicable to build a shunt for 25,000 ampères.

We come now to the instrument itself. A sensitive millivoltmeter is used to measure the drop. The condition for maximum sensitiveness would require that all of the resistance of the instru-

ment be in the armature of the d'Arsonval type so generally used. And in order that a given resistance may afford as many ampère turns as possible without making too heavy a bobbin, the material must be one low in specific resistance, such as copper. The use of copper means a high temperature coefficient, and in order to keep within one per cent. on large switchboard ammeters it is always necessary to correct for instrument temperature. The largest size of instrument—independent of capacity, as change of size for current rating is made in shunt and not in instrument—has a temperature coefficient corresponding to that of pure copper, or about two-tenths of a per cent. per degree Fahrenheit. The smaller types are lower in temperature coefficient, as the lighter movement gives the instrument designer more leeway. In high resistance instruments, such as voltmeters, there is a series coil which is made of low temperature coefficient alloy, which forms so large a proportion of the total instrument resistance that the coefficient of the whole is negligible.

One of the most important sources of error is the magnetic effect of stray field in the immediate vicinity of a bar carrying several thousand ampères. Instruments should never be placed within two feet of such bars. The iron shield usually provided is not only likely to be faulty as a filter for lines of force of such density, but consequent poles are formed in the case itself. The writer has found instruments placed in the vicinity of a stray field of such strength that he could hang his bunch of keys from the case.

The resistance of the leads is generally some five per cent. of that of the instrument, and the screw connections must be kept clean. If it is found necessary to lengthen the leads, care must be taken that the resistance is kept constant by a proportionate increase in size of wire used.

The leads should be twisted and kept from swinging loosely in the presence of stray field. Otherwise there is a dynamo action which the millivoltmeter is sensitive enough to indicate by a pulsating needle.

When several high capacity ammeters are in use, it is advisable to have them interchangeable. Instrument makers will so furnish them at little or no extra cost. The shunts are sawed until they all have the same drop per thousand ampères, and then the resist-

ance in the leads is adjusted to bring the instrument resistances to a common figure. The various instruments may be checked at any time by connecting them to the same shunt. Of course this does not check the shunts, but any trouble is much more likely to be in the instruments. Connections should also be arranged, if possible, to put the shunts in series, when they too may be checked.

DISCUSSION.

PROF. BURGESS: I have been asked to discuss this, but it doesn't seem to me that any discussion is necessary. It is a very useful paper, since it points out to those who are to use ordinary instruments what degree of accuracy they may expect, and what precautions are to be observed. In this respect it is a very useful paper. I would suggest a correction to the statement which says "one per cent. may be taken as the limit of accuracy of the best type of switchboard ammeters." That undoubtedly means a limit of error of one per cent.

PRESIDENT BANCROFT: While a good many of us may never be put in a position where these problems come up, it certainly is of great value to have a definite statement of the sources of error in instruments and the methods of eliminating or neutralizing them.

DISCUSSION.

(*Communicated after the meeting, by Mr. Addicks.*)

In reply to Prof. Burgess' criticism, I quote the following from Holman on "Discussion of the Precision of Measurements," Wiley, 1894, page 13.

"By the accuracy of a result we mean its freedom from error. The real measure of the accuracy of a result is, therefore, the error of that result. Thus, if we knew that a result had an error of 2 per cent. we should say that it was *accurate* to 2 per cent., or we might say that its accuracy was 98 per cent. The latter phrase, although more exact, is less common and convenient than to say that the accuracy was 2 per cent."

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 20, 1905, President Bancroft in the Chair.

THERMODYNAMICS OF THE ELECTRIC INCANDESCENT LAMP

By E. F. Roeber.

Investigations tending towards the invention of new incandescent lamps involve with necessity high-temperature chemical research work. This indicates the intimate connection of such researches with electrochemistry.

The recent development of several new types of incandescent lamps should, therefore, attract the interest of the electrochemical fraternity in general.

For this reason I accepted with pleasure a suggestion to bring before the members of the Society the most important and promising new types of incandescent lamps—several of which are shown here to-day for the first time in public in this country—and to present a brief summary of the thermodynamics of radiation, as applied to electric incandescent lamps. The fundamental assumption is here made that the radiation given off from an incandescent lamp filament is strictly "thermal radiation," for on this assumption depends the application of the two principles of thermodynamics. This assumption excludes any such effects as fluorescence.

From a theoretical point of view the simplest electric incandescent lamp is a direct-current lamp with its filament in an absolute vacuum. We will assume the filament to be a conductor of the first class, *i. e.*, of the type of metallic conductors. The heat which is conducted away through the leading-in wires shall be assumed to be negligible.

Under these conditions there can be no loss of heat by conduction or convection, and if we neglect the energy which is consumed in throwing off particles of carbon from the filament, etc., the whole electrical energy which is supplied to the lamp must be changed into energy of radiation.

For the sake of simplicity the filament may be assumed to be a straight cylinder of the length l cm., and with a circular cross-

section of radius r cm. Let γ be the conductivity of the materials of which the filament is made. Then the conductance is $\gamma \frac{r^2 \pi}{l}$ mhos, and if e is the voltage at the terminals of the filament, the current in ampères is $e \gamma \frac{r^2 \pi}{l}$ and the power supplied to the lamp in watts is $e^2 \gamma \frac{r^2 \pi}{l}$, hence the energy radiated per second from one square cm. of surface of the filament is $\frac{e^2 \gamma}{2} \frac{r}{l^2}$ watts.

This is at least the case when the stationary condition has been reached. In the first time element after the circuit is closed, the electrical energy which is supplied to the lamp is used to raise the temperature of the filament, and the temperature will continue to rise until it reaches that value for which the total energy radiated equals exactly the electrical energy supplied to the lamp.

For a given filament and for a given temperature of the surroundings the total energy of radiation depends on the temperature of the filament only, and if we introduce the further assumption that the filament is a perfectly "black body" (*i. e.*, according to Kirchhoff's definition, one which absorbs all radiations falling on it, and neither reflects nor transmits any), we can directly apply the Stefan-Boltzmann law.[1]

According to this law, the total energy of radiation from a black body equals $K (T^4 - T_0^4)$, where T is the absolute temperature of the radiating filament, T_0 the absolute temperature of the surroundings, and K the so-called radiation constant.[2]

In our special case we, therefore, get

$$\frac{e^2 \gamma}{2} \frac{r}{l^2} = K (T^4 - T_0^4) \tag{1}$$

This equation enables us to calculate the temperature of the filament if the voltage e at its terminals is given and if it behaves as a black body.

Now this total radiation consists of electro-magnetic waves of an infinite series of different wave lengths, but the physiological effect of light is produced on the normal eye only by those waves the length of which is between 8×10^{-5} and 4×10^{-5} cm, or the

[1] Stefan, Ber. d. K. Akad. der Wissensch., Wien, *79B*, 2 Abth., 391 (1879); Boltzmann, Wiedemann's Ann., *22*, 291 (1884).

[2] For numerical determinations of K, see F. Kurlbaum, Wiedemann's Ann., *65*, 759 (1898).

frequency between 39×10^{13} and 76×10^{13} periods per second.

The endeavor must be to get such a spectrum of the incandescent filament radiation that as much as possible of its area falls within the limits of the wave lengths of visible light.

A first indication of the degree to which this desideratum is filament must be 4,900 degrees absolute, or over 4,600 degrees C. the product of the wave length λ_m of maximum energy and the absolute temperature T of the radiating source is a constant;

(2) $$\lambda_m T = \text{const}$$

If the wave length λ_m is measured in centimeters, the constant[4] in equation (2) is 0.2940 for a black body.

If, therefore, the temperature of the incandescent filament increases, the maximum of energy is shifted toward shorter wavelengths. In order to get the maximum energy within the visible spectrum, for instance at the wave length 6×10^{-5} cm. not far from the D line of sodium, the absolute temperature of the black body filament must be 4,900 degrees absolute, or over 4,600 degrees C. This is far beyond anything we can hope at present to reach in incandescent lamps.

The spectral distribution of energy in the radiation of a black body is given by Wien's law.[5]

(3) $$J = c_1 \lambda^{-5} e^{-m}$$

$$\text{and } m = \frac{c_2}{\lambda T}$$

where J is the energy corresponding to the wave length λ (region of spectrum λ to $\lambda + d\lambda$), T is the absolute temperature of the radiating black body, e is the base of the natural system of logarithms, and c_1 and c_2 are constants. This equation has been modified by Planck.[6] Planck's law which has been found to represent in a most remarkable way the facts throughout the extreme ranges in which it has been tested, reads as follows:

(4) $$J = c_1 \lambda^{-5} \frac{1}{e^{m} - 1}$$

$$\text{and } m = \frac{c_2}{\lambda T}$$

[3] Wien, Wiedemann's Ann., *46*, 633 (1893;) *52*, 132 (1894).
[4] Lummer & Pringsheim, Verh. d. Deutsch. Phys. Ges., *1*, 218 (1899).
[5] Wien, Wiedemann's Ann., *58*, 662 (1896).
[6] Berichte der K. Akademie d. Wissenschaften, Berlin, 544 (1901).

These formulas represent the fundamental laws of the radiation of a black body. For a more extended summary and analysis of these laws the reader may be referred to the original papers, referred to above, or to a very suggestive serial by O. Lummer, in *Zeit. f. Beleucht.*, 1904; or to the excellent discussion by A. L. Day and C. E. Van Orstrand in the *Astrophysical Journal*, v. 19, p. 1, 1904, or to the concise summary by C. W. Waidner and G. K. Burgess in the *Bulletin of the Bureau of Standards*, 1905, No. 2, p. 197. The latter paper is a most useful summary of the methods of optical pyrometry, and its study is strongly recommended to those metallurgists who desire to measure high temperatures by easy and exact methods.

It would, of course, be possible to calculate from Planck's law (4) the exact distribution of the energy in the spectrum of a black body at any given temperature, or to calculate from this law the temperature at which the energy within the visible spectrum becomes a maximum. This would give us the temperature for which we would get the highest possible efficiency of a black body filament incandescent lamp.

However, no attempt is here made to give this calculation, for two reasons. First, from Wien's displacement law we found already approximately this temperature which is very high, beyond anything we can hope to reach in practice. Secondly, we will see later on that a black body filament is really not the goal to strive at, in incandescent lighting.

In practice the efficiency of a lamp is not given as the ratio of the energy of radiation within the visible spectrum to the total radiation, but is given by the candle-power which is produced by one watt, or what is the more general, although improper commercial usage, by the reverse ratio, *i. e.*, the number of watts consumed per candle. The rays within the visible spectrum form what we call the flux of light, and their energy is sometimes assumed to be measured by spherical candle-power.

The underlying idea is that the spherical candle-power is proportional to the energy of the light emitted. Now, as long as we have to do with light of one single wave length this supposition is correct. But if we compare two composite sources of light, the

element of the physiological effect enters into the measurement of the candle-power since the intensity of the physiological effect depends on the wave length. On the other hand, the energy of light has a distinct value independent of whether it produces any physiological effect or not.

It is, therefore, strictly correct only with monochromatic light to assume the candlepower to be a measure of the energy of visible radiation; and for this reason it is proper only for single wave lengths to try to find a numerical relation between spherical candle-power and the usual units of power—or as we may say the mechanical equivalent of light.

Since the physiological effect on the normal eye is a function of the wave length, the relation between candle-power and other units of power must also be a function of the wave length.

Nevertheless, in practice we compare different sources of light—of different spectral composition—by their candle-power. In such cases we average the physiological effects of the energies of the different wave lengths.

The results obtained by experimental determinations of the mechanical equivalent of light, if not limited to a single wave length, must, therefore, be taken *cum grano salis,*[7] although they undoubtedly are interesting as giving a first approximation to the truth.

Experimental researches on this problem have first been made by J. Thomsen and O. Tumlirz.[8] The result of Tumlirz was 0.188 watt per spherical hefner candle. However, his method of measurement was open to objections, since he separated the visible spectrum from the other rays by trying to absorb the latter in a layer of water. This must lead to too high a numerical value of the watts per candle, as was more recently pointed out by K. Angström[9], who made another determination of the mechanical equivalent of light. In order to separate the visible spectrum from the balance of the spectrum, he decomposed by refraction the total radiation into the rays of different wave lengths, cut off all rays except those with the visible spectrum, and recombined the latter

[7] See, for instance, C. J. Reed, Electrical World and Engineer, *36*, 170 (1901), also the editorial in the same volume, 247.

[8] See the summary of their researches in an article by C. Hering, Elec. World and Eng., *37*, 631 (1901).

[9] K. Angström, Physik. Zeit., *3*, 257 (1902).

by means of a lens. His result appears to be the best available at present.

Angström found that the equivalent of the light radiation of 1 hefner candle per square cm. at a distance of one meter (one meter candle) is 8.1 ergs per second. This gives as the equivalent of one spherical hefner candle 0.102 watt. This is almost one-half the equivalent of Tumlirz.

Now one spherical hefner = 0.88 spherical (British) candle power. We, therefore, get as the result of Angström's determination, for 100 per cent. of efficiency

1 spherical candle-power = 0.115 watt,

or

1 watt = 8.63 spherical candle-power.

One of the most efficient new types of incandescent lamps, the tantalum lamp, consumes initially 1.99 watts per mean horizontal candle-power and 2.78 watts per mean spherical candle-power; while the average value throughout life was found as 2.19 and 2.70 watts, respectively, according to recent tests made in a testing laboratory in this country. For the efficiency calculation the watts per spherical candle-power must be chosen, and if we base this calculation on 2.70 watts and on Angström's equivalent, it follows that the tantalum lamp has an efficiency of 4.3 per cent.

An ordinary carbon filament incandescent lamp, if consuming 3.1 watts per mean horizontal candle-power and 3.9 watts per mean spherical candle-power has an efficiency of 3.0 per cent.

A few words should be said in this connection concerning mean horizontal and mean spherical candle-power. It is still a general rule in this country to rate incandescent lamps (with the exception of the Nernst lamp),by means of horizontal candle-power,although the impropriety of this method is clearly recognized. The American Institute of Electrical Engineers has already formally declared itself in favor of rating on the basis of mean spherical candle-power. This is obviously the only proper method of comparing the light given out by different types of lamps with each other.

But even in the test of a single lamp, the curve giving the change of horizontal candle-power during life does not represent a true indication of the performance of the lamp. In testing the horizontal candle-power one unconsciously makes the silent supposi-

tion that the reduction factor (by which the mean horizontal candle-power must be multiplied to get the mean spherical candle-power) remains the same during the whole life. But as a matter of fact, this is not the case. The distribution of light in a vertical plane changes during life, and with it changes the reduction factor.

This was very clearly shown in the tests of the tantalum lamp above referred to, and is directly indicated by the figures given above. In this case a black band was formed during life on the globe around the sides of the bulb and about an inch wide. This materially decreased the horizontal candle-power.

We have now reached the problem: What can be done to make incandescent lamps more efficient?

One obvious conclusion from the above discussion is, that if we want to employ a black body filament we must increase the temperature of the glowing filament very materially.

The carbon filament of the old ordinary incandescent lamp has often been assumed to come pretty near a black body. Now, it will at once be seen, that we can easily increase the temperature T of the filament by increasing the voltage *e;* equation (1) gives the exact variations of T with *e*. If we do this, the maximum of energy in the spectrum will be shifted towards shorter wave lengths according to (2); *i. e.,* the light gets better, whiter, more like sunlight in spectral composition. As a necessary concomitant, the area of the energy curve, which falls within the visible spectrum, increases; in other words, the efficiency increases.

It can be laid down as a general rule that the color effect of the light of an incandescent lamp enables one to judge approximately the efficiency at which it burns. The reason is that according to the above theory, both the color effect and the efficiency are functions of the temperature. In a private communication to the writer, Dr. Louis Bell gives the following color scale of efficiencies of ordinary carbon filament incandescent lamps. Naturally, these are only approximations, since, as Dr. Bell points out, one's judgment is so liable to be warped by the bluish tint of ordinary daylight, owing to reflected sky light that the color value of artificial light are very difficult to judge.

Watts per c. p.	*color.*
1.5	clear white.
2.0 to 2.5	white very faintly tinged with yellow.
3.0	yellowish white.
3.5	yellowish.
4.0	yellowish tinged with orange.
4.5	orange yellow.
5.0	distinctly orange red.

Lummer[10] refers to a test of a lamp of 16 spherical candle-power, which, when operated at 45 volts, gave 16 candle-power and consumed 3.5 watts per spherical candle-power; the voltage was raised, and with it the electrical power supplied to the lamp to 285 watts; simultaneously the candle-power increased to 2,000 candle-power, representing a consumption of 0.13 watt per spherical candle-power (which is almost the theoretical limit according to Angström's equivalent). Thus an increase of energy in the ratio from 1 to 5 corresponds to an increase of candle-power from 1 to 130, and to an increase of efficiency from 1 to 26.

This experiment lasts, however, but a span. This brings us to the point of life. We must make in practice a compromise between a reasonably long life and a reasonably high efficiency. There must be an economic relation between life of lamp, cost of lamp and cost of energy. This relation was first given in exact mathematical form by W. D. Weaver.[11]

Moreover, another important forward step in the manufacture of the carbon filament lamp was the recognition[12] of the importance of differentiating useful life from actual life. This is due to the continual decrease of candle-power of the lamp, setting in shortly after starting; accompanied by an increase in the consumption of watts per candle-power. It is now considered proper practice to "oslerize" a lamp when its candle-power has decreased to 80 per cent. of its initial value.

The decrease of candle-power at constant voltage which determines the useful life of the carbon filament lamp is known to be

[10] Lummer, Zeit. f. Beleucht., March 20, p. 97 (1904).

[11] W. D. Weaver, Van Nostrand's Eng. Mag., 1885; The Electrician and Elec. Eng., April, 1885; September, 1885, and June 3, 1891.

[12] J. F. Marshall, Journal Franklin Inst., July, 1905, p. 43. The necessity of oslerizing lamps was first strongly advocated in this country by Carl Hering in a paper before the Amer. Inst. Elec. Eng., March, 1893, on the basis of a method suggested by O'Keenan.

mainly due to three causes,[13] first an increase of resistance, resulting in a diminution of watts; second, a change in the surface activity of the filament, resulting in a diminution of emissivity; third, diminished translucency of the globe, due to the well-known black deposit which forms on the globe. A possible explanation of the second effect will be discussed later. Concerning the third effect it may be said that it is usual to speak of evaporation of carbon. But I am not aware that it has ever been proven that such evaporation really takes place. It is quite possible that minute small solid particles of carbon are thrown off from the filament. It is a fact that the carbon is mainly given off near the negative extremity of the filament. Chemical analysis of the black deposit in the case of lamps with flashed filaments have shown that the deposits consist partly of carbon and partly of hydrocarbons.

According to Marshall 16 candle-power carbon filament lamps can be made according to the following table:

useful life in Hours.....	28	132	412	1,000	2,005	3,570	6,125
Watts.....	32	40	48	56	64	72	80
Watts per c. p.....	2	2.5	3.0	3.5	4.0	4.5	5.0

What type to select depends on the relative cost of the lamps and of the electrical energy.

We will return now to a discussion of possibilities of improving the efficiency. If a black body filament is to be used, the progress must be looked for in an increase of its temperature. This is the reason for trying metals of very high melting points for filaments; such as osmium in Dr. Auer von Welsbach's osmium lamp, since osmium has the highest melting point of any known metal. The same principle was followed in the systematic development of the tantalum lamp of the Siemens & Halske Co., by Dr. von Bolton, who tried the following metals one after the other: vanadium, niobium, tantalum. Their melting points are 1,680°, 1,950° and 2,250 to 2,300° C., respectively. On account of its highest melting point tantalum was finally chosen. The under-

[13] Houston & Kennelly, Electric Incandescent Lighting, p. 176.

lying idea is that a filament made from a material of a very high melting point will stand without injury a high temperature during a reasonably long life.

However, by simply increasing the temperature we cannot get very far towards the realization of the ideal if a black body filament is used. We saw before that according to Wien's displacement law, we would need to use a temperature of more than 4,600° C., *i. e.*, more than 8,000° F., to get the maximum of energy at 0.6 μ. There is no hope of coming near such a temperature in present practice.

But, fortunately, there is no necessity whatever to use a black body filament. A black body is an ideal case in thermodynamics; it is nowhere strictly realized in practice, but it is absolutely within the grasp of the mathematical physicist. However, the black body is not at all the ideal thing for the lighting engineer. On the contrary, we will see that the further we can get away from the black body, the better for us.

The above discussion was based on the consideration of the black body filament, because on this matter we can speak with certainty and without vagueness. The discussion of filaments departing from black body radiation can be carried out only in special cases with similar mathematical exactness. In general, we must be satisfied to indicate the direction in which the results will vary from black body radiation.

At a given temperature the total radiation from a non-black body is less than from a black body. Hence, if we substitute a non-black body filament for the black-body filament, leaving everything else unchanged, our fundamental equation (1) will no longer be valid. The stationary condition represented by the equality of radiation energy and electrical energy supply, necessitates now a higher temperature T than with a black-body filament.

Of greater importance, however, than the total radiation is the distribution of the energy of radiation over the whole spectrum. Non-black body radiation is essentially selective radiation. The real ideal thing about the black body is that, according to definition, its radiation is not selective, since it absorbs all rays of any wave length, and, therefore, according to Kirchhoff's law of the parallelism between radiation and absorption, it also radiates all of them.

The ideal filament for the lighting engineer must be one which absorbs only rays within the visible spectrum, while it either perfectly reflects all other rays or is perfectly transparent for the same. Such a body would then emit a radiation completely within the visible spectrum.

It serves no useful purpose to speculate, whether we have any prospects to realize such an ideal filament body. Instead we may briefly state what we know concerning polished platinum, which is one of the bodies which of all those tested show the greatest departure from a black body.

In Wien's displacement law (2) $\lambda_m T = const$, the constant is 0.2940 for the black body and 0.2626 for polished platinum (Lummer and Pringsheim), when the wave length is measured in cm. Hence the absolute temperature T at which the maximum of energy lies at a certain wave length, is less by about 10 per cent. with polished platinum than with the black body. This means that heated to the same temperature, a polished platinum filament will have a spectrum with its maximum of energy nearer to the visible spectrum than a black body filament. Nevertheless, polished platinum is still very far from the ideal material which the lighting engineer must aim at.

No rule can be laid down how to devise such an ideal material, except to determine empirically the absorption of all possible substances for all different wave lengths.

However, the degree of departure of a body from black body radiation does not depend solely on its material; it also depends to a certain degree on the condition and the configuration of its surface. The more porous a body the more will it behave like a black body.[14]

The realization of the black body in practice is based upon Kirchhoff's fundamental rule that the radiation inside an enclosure all points of which are kept on uniform temperature is absolute black-body radiation. The black body with which the laws of radiation have been experimentally established is such a hollow inclosure, the walls of which are kept on uniform temperature, but contain a small opening through which the radiation is absorbed. The presence of the opening represents a negligible departure from absolute black-body radiation. Further, in pyro-

[14] F. Blau, Elektrotechnische Zeitschrift, Feb. 23, 1905, concerning the osmium lamp.

metric practice, "if a porcelain tube with closed bottom be immersed into a lead-hardening bath, the radiation coming from the bottom of this tube will be a close approximation to that of a black body, especially if the inside of the tube is blackened with iron or nickel oxide, for example."[15]

Now it is evident that any pore in the surface of an incandescent filament whatever it is made of will behave more or less like a black body. Hence we get the important result that the ideal filament must have a polished surface without pores.

In the case of the osmium lamp it has been noticed that the initial increase of candle-power which is observed with almost every filament after the current is turned on, continues for an unusually long period, somewhat like 200 hours. This is said to be due to a continuation of formation of the filament, the particles being better fused together and the surface getting more polished. It is quite possible that in the case of the new graphitized filament of the General Electric Company something similar goes on, since the treatment is essentially an external surface treatment, although the material of the filament itself is also changed. Of course, this explanation only holds good if an original departure from the black-body condition can be experimentally proven.

While speaking of the ordinary carbon filament, it was noticed above that two of the reasons of the ageing of the lamp were decrease of surface emissivity and a throwing off of carbon particles from the filament, with a resulting blackening of the globe. These two effects have generally been considered to be independent of each other, although in the light of the above discussion it may be that the decrease of emissivity is due to the formation of pores or minute holes in the surface of the filament, as a result of the throwing off of small carbon particles. If this is true, the negative terminal of the filament (from which the carbon particles are mainly thrown off) should lose more in emissivity than the other terminal. I do not know whether experiments of this kind have been made. To test this suggestion it would be necessary, of course, to carefully separate the effect of change of emissivity from the effect of blackening of the globe. For this reason the globe would have first to be uniformly cleaned, before

[15] Waidner and Burgess, Bull. Bureau of Standards, *1*, No. 2, 196 (1905).

the emissivity of the two ends of the filament should be compared. Of course, here the supposition is again made that the carbon filament is originally different from a black body.

These are the principal points which I wanted to bring out concerning the results of the thermodynamics of radiation, as applied to the electric incandescent lamp.

It gives me now pleasure to show you the new types of lamps which for this purpose have been placed at my disposal. Thanks to the courtesy of Mr. Edward D. Adams, I am enabled to show you two types of the tantalum lamp made by the Siemens & Halske Co., in Berlin. For the osmium lamps made by the Gas Incandescent Lighting Co., of Berlin, I am greatly obliged to the inventor, Dr. Carl Freiherr Auer von Welsbach in Vienna, and to Mr. Sidney Mason, president of the Welsbach Co., in Philadelphia. Through the courtesy of Mr. John W. Howell I am enabled to show you three types of the new graphitized carbon filament lamp made by the General Electric Co., and invented in its research laboratory under the direction of Dr. W. R. Whitney.

Concerning the manufacture of the tantalum lamp, von Bolton[16] gives the following information on the manufacture of the tantalum lamp. He first mentions the experiments of Berzelius and Rose. They produce tantalum by heating the potassium fluoride (K_2TaF_7) with potassium, and extracting the potassium fluoride with water, but this method does not yield pure metallic tantalum, the product contains only 5 per cent. of the pure metal. Moissan described in 1902 the production of tantalum in the electric furnace by reducing the oxide with carbon; but this metal contained about 0.5 per cent. carbon, and was therefore either a carbide (0.5 per cent. C. being a pretty large quantity in view of the high atomic weight of tantalum) or it was an alloy of the metal with carbide. Von Bolton describes briefly two methods of producing pure metallic tantalum.

[16] Zeit. f. Elektrochemie, Jan. 20. The principal literature on the tantalum lamp, besides a great many unsigned articles in various technical journals is contained in the following papers: von Bolton, Zeit. f. Elektrochemie, Jan. 20; von Bolton and Feuerlein, Elek. Zeit., Jan. 26; Kennelly & Whiting, Elec. World and Eng., March 25; Siedek, Zeit. f. Elek. (Vienna), May 7; Bell & Puffer, Elec. World and Eng., June 3, 1905; Bell, paper read before the National Elec. Light Asso., June, 1905. Concerning the occurrence of tantalum minerals, see Day, *Electrochemical and Metall. Industry,* April, 1905.

The first method is electrolytic reduction of one of the oxides in the incandescent state in a vacuum. He formed filaments of brown tantalum tetroxide and placed them in vacuum. By passing the electric current through, they were caused to glow slightly, whereby much air was driven out of the porous filaments. Evacuation was then continued and the temperature of the glowing filament was increased until, at beginning white heat, several points of the filament showed strong incandescence. These points gradually extended to longer and longer lines, until the filament was incandescent uniformly along its whole length. During this reaction much gas was given off, which was identified as pure oxygen. The brown color of the original oxide had changed into pure metallic gray, and the wire had become flexible after several hours of strongest white incandescence, like a wire of copper.

The second method (U. S. patent 799,441, September 12), which is the more practical one, is to produce tantalum by the method of Berzelius and Rose mentioned above, and then to purify and refine the metal in the vacuum under the action of the electric arc. This method is based on the fact that the oxides of tantalum melt more easily than the tantalum itself, and on the other fact that they are much more easily volatilized in a vacuum than the metal, so that the metal can be completely separated from the oxide.

Concerning the manufacture of the filament of the osmium lamp, the latest information is given by Blau.[17] The starting material is very finely divided osmium, which is mixed with organic binding materials so as to form a thick, tough paste, which is pressed under very high pressure through an aperture. A thread is thereby obtained which is formed into loops. The threads are then dried and are heated in the absence of air in order to carburize the binding material, and then subjected to the most important process which is called formation. The threads which now consist of porous rough osmium, with a high content of carbon, are heated for a long time by means of an electric current gradually to a higher and higher temperature up to white heat in an atmosphere which contains very much steam and

[17] Elektrotechnische Zeit., Feb. 23, 1905, is the last account of the results obtained by the company which makes this lamp. Concerning the osmium lamp in England, see Lond. Electrician, May 12, 1905.

smaller or larger quantities of reducing gases. The carbon is removed by the same reaction which takes place in the production of water gas, and the filament thus becomes pure porous osmium of a far greater density than the former rough thread. During the first period of the use of the lamp the osmium surface becomes gradually smoother and more polished. This accounts for an increase of the light given out by a lamp during this period.

With regard to the manufacture of graphitized carbon filament of the General Electric Company,[18] the chief point is that the ordinary treated filament of the carbon incandescent lamp is subjected to additional processes, especially heating the filament in the electric tube furnace at a temperature of from 3,000 to 3,700 degrees C. This "firing" is performed both before and after treating. I have here samples of filaments, one set being treated only, and the other set being treated and fired. The firing results in the production of an exceedingly pure form of carbon, with a considerably smaller specific resistance and greater density than the present filament. By the firing, the temperature coefficient is changed from negative to positive, that means the filament behaves now like a metal, and for this reason it is called a "metallized" filament.

It will thus be seen that in the development of all three new lamps, electrochemical methods have proven of enormous importance.

Without going into a discussion of the probable commercial effect of the new lamps on the electric lighting industry—which is outside of the sphere of this paper and of this Society—it may be simply said that the osmium lamp and the tantalum lamp have reduced by 40 to 50 per cent. the consumption of power per candle-power by the ordinary incandescent lamp. However, for commercial purposes quite a number of other factors would have to be considered.

In spite of the prediction which has sometimes been made in the past that the carbon filament would be doomed, it becomes more

[18] Paper by John W. Howell, before the American Inst. of Elec. Eng., Ashville meeting, June, 1905; paper by Francis W. Willcox, before the Ohio Elec. Light Association, August, 1905.

and more probable that it is still destined to a very long commercial life. With the new graphitized carbon filament, the consumption of power per candle-power has been reduced by 20 per cent. The carbon lamp is in the hands of its friends.

In view of the foregoing discussion it would be extremely interesting to know how far the progress achieved by the new lamps is due to the increased temperature and how far to a greater departure from black-body radiation. We know of all three lamps that their filaments are at higher temperature than the ordinary carbon filament. Concerning the question, however, how far the three new filaments (in comparison with the ordinary carbon filament) depart from the black body, no information of an exact nature has been published to my knowledge.[19]

A complete investigation of these problems would involve not only a determination of the actual temperatures and of the "black body temperatures" of the filaments, but the actual distribution of the energy within the spectrum.

This would give us directly the absolute efficiency of the new lamps as the ratio of the area within the visible spectrum to the area of the total spectrum of the energy curve. It is quite possible that the numerical value of the efficiency, thus determined, may differ essentially from the efficiency, as determined from the candle-power per watt on the basis of the mechanical equivalent of light.

The first definition is absolutely physical and leaves the physiological aspect of the problem out of consideration. In this definition each watt corresponding to one wave length within the visible spectrum is considered as perfectly equivalent to one watt corresponding to any other wave length with the visible spectrum, although the physiological effects may be very different. The second definition of efficiency, on the other hand, is essentially based on the physiological effect. According to the second definition the efficiency of the osmium lamp is practically twice that of the ordinary carbon lamp; but this does not necessarily mean that the efficiency according to the first definition has also been doubled. For the actual efficiency the loss of heat by conduction

[19] Concerning carbon filaments, see the paper by E. L. Nichols, in *Physical Review*, September, 1905, p. 147.

through the leading-in wires is also a factor. This has not been considered at all in the above discussion.

At all events, in spite of what has already been accomplished, it is evident that we are still far from finality. It may be hoped that the progress made in electrochemical methods during the last decade will continue to react on the invention of incandescent lamps in an encouraging and helpful manner, as has already been the case with the three lamps which I had the pleasure to show you to-day.

DISCUSSION.

President Bancroft: I am sure we are all very much indebted to Dr. Roeber for the time and trouble he has taken in getting up his Exhibit, and also to those who have made such an Exhibit possible.

In the last number of the *Zeitschrift für Elektrochemie*, there was an announcement that before long pure magnesia tubes and crucibles would be on the market; and it occurred to me that it was quite possible that one could take a magnesia pyrometer tube and a couple made of pure iridium and pure tantalum and extend the upper limit of our pyrometric measurements very considerably indeed. I ask Dr. Roeber if he knows anything about any experiments bearing upon this, or about the possibility of any such being made.

Dr. Roeber: In the announcement to which Dr. Bancroft refers there is one point of special interest, that is the statement that even at the highest temperatures pure magnesia articles do not show a trace of electrolysis. I understand this to mean that pure magnesia does not conduct the current. This is interesting in connection with the composition of the Nernst lamp filament. I think Mr. Hering has made some experiments on pure magnesia as a non-conductor.

Mr. Carl Hering: I made some experiments with pure magnesia, but I could not get it to conduct, although I heated it to a white heat and applied a very much higher voltage than that used in practice. The heat was so intense that the end of a fine platinum wire melted to a globule.

PROF. FRANKLIN: I had the same experience with pure magnesia.

PRESIDENT BANCROFT: In that case, that would make a very ideal combination. If one could extend the temperature range—even if only to 1,800° or 1,900°—it would cover the whole of the steel problem.

DR. ROEBER: Many metallurgical engineers are still under the impression that optical pyrometers are delicate and difficult to handle; as a matter of fact, optical pyrometry is comparatively very easy, and there are now several reliable instruments on the market. The excellent and concise summary of Waidner and Burgess on optical pyrometry, published by the Bureau of Standards in Washington, should deserve thorough study by metallurgists. Up to the present all furnace operations have been dependent on the trained eye of the furnace man. His experience is locked up in his trained eye, and that cannot be "mummified." But by means of optical pyrometry we can get to the same result, we can reduce furnace practice to a record which is permanent. The whole range of temperatures used in iron and steel metallurgy is now within the realm of optical pyrometry. Thus Wanner, whose high-temperature pyrometer is well known, has recently devised a low-temperature instrument, to be used, I believe, between 600° and 1,000° C. and specially adapted for tempering steel. This instrument is also interesting in connection with the paper under discussion, since a small osmium lamp is employed as comparison lamp. This is the first commercial application of the osmium lamp in this country.

PRESIDENT BANCROFT: Is it possible to determine cooling curves by means of an optical pyrometer and get satisfactory results?

PROF. FRANKLIN: I would merely say that the temperature can be accurately measured by optical pyrometers; and that, of course, is all that you need ask.

DR. ROEBER: With the most types of optical pyrometers, it would be somewhat difficult to render them recording instruments. I don't think there are any recording optical pyrometers on the market.

PRESIDENT BANCROFT: I was not aware of any cooling curve having ever been made with the optical pyrometer, and I won-

dered whether any one in the audience had any knowledge bearing on that. Mr. Roeber says that the steel problem is entirely covered by the optical pyrometers. To a certain extent that may be true; but at present we do not know the true freezing point of iron; we do not know what phases are stable, nor at what temperatures they are stable, nor how many phases there are. It seems to me that there is a field yet to be worked out. The apex of the field lies well above the region which we can reach at present with the ordinary pyrometric methods. If the optical pyrometer can be used for these experiments we are all right; if it cannot, we have got to get some development in the use of a pyrometric method with iridum and tantalum, or some other pair of metals, as a means of measurement.

PROF. FRANKLIN: It seems to me the problem you mentioned can be entirely solved and an optical pyrometer made available for these cooling curves by using a larger and larger mass of material in cooling, so you have plenty of time to make the observations. Most other pyrometers indicate more quickly, and therefore permit the following of the curve of a smaller mass of material. If you use a larger amount of material it will enable you to follow the changes, no matter how slow the indication may be.

PRESIDENT BANCROFT: My feeling has been that there would always be danger of the external surfaces being of a different temperature from the mass of the metal, and the optical pyrometer shows you merely the temperature of a surface film.

PROF. FRANKLIN: That would also be covered by providing for sufficiently slow melting. You could arrange to have the difference of temperature between the interior and surface as small as you please, if you cool slowly enough. It is merely a matter of rapidity or slowness of cooling, if it is slow enough you can secure an even, uniform temperature, as nearly as you please.

PRESIDENT BANCROFT: That is quite true; but you get your slowness in cooling either by supplying heat or by very effective lagging. Can you get a very effective lagging and yet have an opening through which you can inspect that particular portion? Will there not always be a much greater radiation of heat at the point on which you set your pyrometer than in the other portions of the metal?

PROF. FRANKLIN: Not necessarily, because the optical pyro-

meter is at its best when you are looking at a hole into the material; and therefore the spot which is radiating heat to you happens to be the one that you care most to know the temperature of.

Dr. J. W. Richards: I have not used the Wanner pyrometer for determining the temperature of a cooling body such as you mention; but I have followed the cooling of the interior of a furnace after the supply of heat was shut off. It takes about a minute to adjust the Wanner pyrometer to the readings; so that the cooling of the interior of a furnace—for instance, a Bessemer converter that has been emptied—can be followed at the rate of about one observation a minute with the modern Wanner pyrometer.

President Bancroft: That would be perfectly satisfactory for the work I have in mind, because at present our rates of cooling with alloys are about one degree per minute. If necessary, we can cool more slowly.

Prof. Franklin: In the case you have in mind I would like to ask whether you can make use of a cavity; or is the substance of which you wish to measure the temperature a melted substance?

President Bancroft: Both cases would probably arise.

Prof. Franklin: When you can employ a cavity the Wanner pyrometer is free from error; and also, the temperature you measure would be that of the interior of the body.

Dr. Richards: In discussing Dr. Roeber's paper one point I would like to ask is this: I understood Dr. Roeber to say that the carbon filament cannot be used, or is not used, at as high a temperature as these metallic filaments; and, also, that the carbon did not volatilize, according to his opinion. If carbon does not volatilize at those low temperatures (its boiling point being probably 3,700° C.), why cannot the carbon filament be used at as high temperatures as these metals of high melting points?

Dr. Roeber: I cannot deny the possibility of the black deposit on the globe being due to vaporization of carbon. But this hypothesis has, as far as I know, never been proven. It is quite possible that the black deposit is due to solid minute particles of carbon thrown off from the filament. The facts that these particles are thrown off in straight lines and that they are preferably thrown off from the negative half of the filament are significant. It may

be that there is vaporization of carbon, but if it occurs, there surely is also some other effect, besides vaporization and different from it.

MR. S. S. SADTLER: What do those solid particles look like?

DR. ROEBER: I have not seen them.

MR. SADTLER: I think observation under the microscope would throw some light on it as to whether they were thrown off by volatilization.

DR. RICHARDS: If thrown off, could they not be screened?

DR. ROEBER: Yes, there is a screening effect; one may distinctly see the "shadow of the negative leg."[1] When the filament is a straight horse-shoe or lies wholly in one plane, the particles thrown off from the negative leg are intercepted by the positive leg in the plane of the filament, so that in this plane the globe is protected. This is then indicated by a line in the black deposit of the globe.

PROF. FRANKLIN: The vapor does not act that way, though.

DR. ROEBER: That is the reason why I think the effect must be different from ordinary vaporization.

DR. RICHARDS: Have the tantalum lamps been used long enough to show what the deterioration of the efficiency of the lamp is due to; and if it does not destroy the tantalum, can the efficiency be regained by a simple mechanical or thermal treatment?

DR. ROEBER: When the lamp is put into use the tantalum filament is of perfectly cylindrical form and is wound loosely around the points of support. During use the surface of the filament changes. Bumps develop on the surface and the filament contracts. When the stress in one leg gets too high, the filament breaks, but this does not always mean that the lamp is now dead. The broken leg may make contact with another leg and the lamp will continue to burn, a portion of filament now being short-circuited. The decreased surface of the active filament for the same energy supply results in an increase of brightness, and may even result in an increase of candle-power.

PRESIDENT BANCROFT: Do I understand that the lamp works better the more broken it is?

DR. ROEBER: No, but it shows that the lamp is normally not used at the highest possible efficiency.

[1] Houston and Kennelly, Electric Incandescent Lighting, page 176, and following.

Dr. Richards: In the metallurgy of the manufacture of osmium there is a very peculiar danger arising from the volatilization of osmium, or osmium oxide; that is, that it is decomposed by water, depositing metallic osmium. I believe that several cases have arisen where workmen in the factory have had a film of osmium deposited upon the eyeball by the moisture of the eye and have become totally blind, without any remedy ever having been found for it. It strikes me, therefore, that a cracked osmium lamp might be a rather dangerous thing to have in close proximity to one, and that, therefore, this caution might go on record—that if an osmium lamp cracks it should be instantly turned off, so that no one exposes his eyes to danger from the vapor which comes from it.

Another point which I think is interesting metallurgically is this: these metals are useful because of their high melting points, and Dr. Roeber has made it clear that the pure metals are absolutely necessary because a small amount of impurity reduces their melting points and renders them inapplicable. It is, in general, true of any metal, that its melting point is reduced by a small amount of impurity; but there are a few cases of alloys of two metals the melting points of which are higher than the melting points of either of the metals of which they are composed. Aluminium and antimony (aluminium melting at 625° and antimony at 630°) have alloys whose melting point is nearly 1,000°. Aluminium melts at 625° and gold at 1,045°; yet there is an alloy of aluminium and gold having a melting point 250° higher than that of gold itself.

I think, therefore, that there is a possibility (investigation only could show) of alloys of these metals possibly having a higher melting point than either of the metals themselves; that is, the alloys of iridium and osmium or tantalum and osmium (in proportions which would have to be discovered), having a considerably higher melting point than either of the pure metals themselves.

Prof. Franklin: I have been very much interested, indeed, in the résumé of the thermodynamics of radiation which Dr. Roeber has given us; and I would like to suggest that, if possible, he make reference to gaseous radiators as being the most promising ones, in that they present the widest departure from the

ideal black body. Gaseous radiation has always seemed to me the most hopeful solution of the problem of efficient production of light from electricity.

There is one aspect of the question of admixture of foreign substances in lamp filaments which, I think, has been very much overlooked. When we consider that all of these lamp filaments are used at many, many degrees below their actual melting points, and when we consider, furthermore, that admixture of impurities always raises the boiling point, it seems that the advantage coming from reduced volatilization might more than compensate for the purely fanciful disadvantage of working the film nearer to its melting point.

That exception that Dr. Richards refers to occurs after you are far removed from the condition of a dilute solution. The first effect of admixture is, however, always to lower the freezing point and raise the boiling point of a substance; that seems to be a theoretical conclusion from which there is no escape.

PRESIDENT BANCROFT: Suppose you add acetone to water: the boiling point does not rise—it falls.

PROF. FRANKLIN: When I studied thermodynamics I believe there was nothing said about acetone.*

PRESIDENT BANCROFT: These remarks of Mr. Franklin apparently apply to an ideal mixture of hypothetical liquids. Under those circumstances I am perfectly willing to admit they have any properties you choose to apply to them.

PROF. FRANKLIN: We will admit in certain cases, at least, impurities raise the boiling point and lower the melting point. When we consider that perhaps the primary cause of the short life of the filament is a disintegration somewhat akin to vaporization it seems likely that certain impurities added to a carbon filament, for example, would increase its life by a preventing the process akin to vaporization; although at the same time it might very materially decrease the melting point of the carbon.

MR. WM. HAND BROWNE, JR.: Has any explanation been offered for the formation of these lumps on the tantalum filament?

* Immediately after the meeting it occurred to me that I had failed to state fully the conditions under which admixture raises the boiling point and lowers the freezing point of a substance. The condition is that none of the foreign substance pass into the vapor phase in the first instance, and that none of the foreign substance in a freezing liquid pass into the solid phase in the second instance. Under the circumstances, the President's reply was entirely just, but I cannot refrain from this further remark that once you know what thermodynamics has to say you cannot escape it.

Is it due to oxidation or to surface tensions, or possibly to volatilization of certain impurities in the filament?

Dr. Roeber: As far as I know, nothing has been published about this point. It is, of course, a fundamentally important question with all incandescent lamps, to know what changes are actually going on in the lamp during life.

President Bancroft: If the Society permits I should like to come back to this question of the volatilization of carbon. If we have no vaporization of carbon at any temperatures that we have reached, why should it not be possible to obtain—for short intervals, at any rate—almost any imaginary temperature by using a heavy carbon rod in a vacuum with a sufficiently high current going through it? I take it that the disintegration does not have the same effect in lowering the temperature that an ordinary vaporization would. It ought, therefore, to be possible to run the temperature up to fabulous figures before the whole of the carbon rod had been deposited as plate on the walls of the containing vessel.

Prof. Franklin: There is one point in Dr. Roeber's paper which bears on the question of the boiling point of carbon. He called attention to the fact that an incandescent lamp suddenly pushed up to extreme voltages has an efficiency which approaches very near to the theoretical maximum efficiency, which according to the thermodynamics of the problem would indicate a temperature of something like 4,600° absolute, and that seems to be above the temperature which you mention as the boiling point of carbon.

Dr. Richards: There are a good many considerations in metallurgy bearing on the question of reduction by means of carbon, which have led me to come to the conclusion (though I have not proved it conclusively) that carbon has a sensible vapor tension at moderate temperatures. I hope within a few years we will have a table of the tensions of carbon vapor down to the ordinary white heat. I think that this vapor tension is probably sensible at temperatures as low as 1,200° and 1,300° C.

Dr. Thatcher: Regarding the question of the relation between volatilization of carbon and efficiency, I wish to state that I happen to know about a Vacuum Tube Lamp—the Moore Lamp—in which carbonaceous material is used, and it is quite

probable from experiments I made in connection with other work on it, that carbon is the active, light-producing agent and that it is *volatilized,* for I found that by the introduction of pure carbon into the tube, you get the same steady, white light as results from the use of complex carbonaceous material, but the efficiency is *no* greater than in the Incandescent Lamp—it requires 3½ Watts per candle, and under some conditions more. Yet if volatilization of carbon is to be expected anywhere, it is under such conditions as exist in this lamp. As evidence in this direction, I may state that the light is white. The Incandescent appears yellow beside it, indicating a very high temperature. The current used is alternating, and about 10,000 volts.

DR. RICHARDS: Has Dr. Thatcher any idea of, or can he state, the temperature at which that volatilization takes place? The carbon filament, I believe, is run ordinarily at about 2,100° C.

DR. THATCHER: There is no filament at all in this lamp. In it a small amount of loose, carbonaceous material is introduced into a long glass tube which is then evacuated. There are, of course, terminals at the two ends, but no filament of any other fixed conductive material between them. When the high tension alternating current is passed through the tube, they get a fine, white light, and if we can expect volatilization at all, it seems to me it would be in a case of that kind.

PROF. FRANKLIN: I would like to ask Mr. Thatcher whether the light of that lamp has been analyzed with the spectroscope, because by such analysis only could the presence of carbon vapor be indicated.

DR. THATCHER: I don't believe it has.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 20, 1905, President Bancroft in the Chair.

ON THE CHEMICAL SEPARATION OF THE EXCITED ACTIVITY OF THORIUM.

By Herman Schlundt and Richard B. Moore.

The compounds of thorium, like those of radium, emit a radio-active gas designated by Rutherford *the emanation.* The physical and chemical properties of the thorium emanation have been extensively investigated by Rutherford[1] and some of his co-workers, by Rutherford and Soddy,[2] and others. In comparison with the radium emanation that of thorium is very short lived, one-half of it undergoing change in about a minute, while nearly four days are required for the change of one-half of the radium emanation. The disintegration products of the thorium emanation are solids, which are likewise radio-active. These solid products are deposited on surrounding objects and thus impart to them a temporary radio-activity, which has been variously termed by different investigators as induced activity, excited activity, and imparted activity. In a strong electric field, however, Rutherford found that the solid products resulting from the disintegration of the emanation are deposited entirely on the negative electrode, making it intensely radio-active. The excited activity thus concentrated on a metallic surface after exposure to the thorium emanation for some hours decays according to an exponential law with the time, falling to half value in eleven hours, to one-fourth value in the next eleven hours, etc. (See curve C, plate 1).

On the other hand, when a body is exposed to the thorium emanation for a short time—fifteen to thirty minutes—the excited activity after removal does not decay at the normal rate, but increases rapidly during the three hours following, passing through a maximum value and then decaying at the normal rate. (See curve A, plate 1). In explanation for the initial irregularity of

[1] Rutherford, Phil. Mag. (5) *49*, 1 (1900).
[2] Rutherford & Soddy, Jour. Chem. Soc. (Lond), *81*, 321, 837 (1902).

the curve for short exposures, Rutherford[3] assumed that two stages are present, and that the first one changes into the second without emitting ionizing rays, while the second, in changing into a final inactive product, gives off the radiations which produce the observed activity. From the long exposure it is seen that in one of the changes one-half of the matter undergoes change in eleven hours. Then by determining the time which elapsed between the beginning of the short exposure to the time of maximum activity, and assuming that both changes follow an exponential law, Rutherford calculated the rate of change of the other stage. He found that its rate was more rapid, one-half disintegrating in approximately fifty-five minutes. Originally, Rutherford[4] assumed that the first product, the inactive stage, changes at the rapid rate, but later,[5] on the basis of experiments by Pegram,[6] he altered this view, assigning the slow rate to the first change. Miss Slater[7] recently also advanced the latter view independently. Her experimental results on the separation of the excited activity of thorium, (1) by the action of the cathode discharge, and (2) heating the products and volatilizing one of them, find a satisfactory explanation on the theory that the first change is the slow one and is not accompanied by ionizing rays. In distinguishing between the two stages Miss Slater uses the same terminology as that applied by Rutherford to the excited activity of radium, naming the first stage Thorium A, and the second Thorium B. Rutherford used the same terms in referring to these products, designating the final inactive product Thorium C. Miss Slater found that Th A can be almost entirely removed from an active wire by heating it to a dull red heat for a few minutes. Th B is left on the wire, the activity of which decays to half value in fifty-five minutes. (See curve B, plate 1).

Previous to Miss Slater's work, von Lerch[8] had succeeded in separating from solutions containing the matter responsible for the excited activity of thorium, radio-active products by both electrolytic and chemical methods. In some instances these prod-

[3] Rutherford, "Radio-activity," p. 270.

[4] Loc. cit., p. 271.

[5] "Present Problems in Radio-activity." Address given to the International Congress of Arts and Science, St. Louis, 1904, Pop. Sci. Mo., *67*, 5 (1905).

[6] Phys. Rev., *17*, 424 (1903).

[7] Phil. Mag. (6), *9*, 638 (1905).

[8] Drude's Annalen, *12*, 745 (1903).

ucts possessed the normal rate of decay, as shown by curve C, but in a number of experiments products were obtained whose rate of decay fell below the normal rate. Pegram[9] in studying the electrolysis of thorium nitrate solutions obtained products with varying rates of decay, but in a majority of cases the products did not decay according to an exponential law. In fact the electrolytic and chemical methods employed by the two last-named investigators apparently indicated the existence of several other constituents of the excited activity besides the two stages assumed by Rutherford.

During the past year, in working on the chemical separation of the types of matter found in ordinary thorium compounds,[10] we found a method of separating from aqueous solutions of thorium nitrate the product Th A. Moreover, the simple assumption of Rutherford, as modified by him and Miss Slater, that the matter responsible for the excited activity of thorium consists of but two stages enabled us to give a satisfactory explanation for the initial irregularity obtained in the curves of recovery and decay of the separated products. We have now applied some of the methods of separation then used to the activity deposited on a negatively charged wire when exposed to the emanation emitted by thorium compounds. The results obtained are embodied in this paper.

Method of Investigation.—Two pieces of platinum foil, 2 x 4 cms. each, were connected to the negative pole of a battery of 200 volts and exposed to the emanation from 20 grams of thorium oxide contained in a metal vessel. The positive pole of the battery was connected to the vessel, which was insulated from the negative electrode by means of a piece of ebonite.[11] After exposure from eighteen to thirty hours the foils were removed and the activity dissolved off by boiling with acids for fifteen minutes after the manner of Rutherford[12] and von Lerch.[13] Three times normal nitric acid was used for the most part, but a duplicate series of experiments was conducted by removing the activity

[9] Phys. Rev., *17*, 424 (1903).

[10] Chem. News, June 9, 1905. The paper embodying the results was presented at the June (1905) meeting of the Am. Chem. Soc. by Professor Calvert. The paper has since been published in Jour. Phys. Chem., *9*, 682 (1905).

[11] See Fig., p. 252, Rutherford, "Radio-activity."

[12] Loc. cit., p. 255.

[13] Loc. cit., p. 752.

from the foils by means of dilute hydrochloric acid (3N). From 75 to 90 per cent. of the activity on the foils was removed by this treatment with acids. The residue on the foils, as well as the residue left on evaporation of the acid solutions, decayed at the normal rate, the activity falling to half value in eleven hours, thus confirming the results of Rutherford and von Lerch (curve A). In carrying out the separations the acid solution was divided into two equal parts for duplicate experiments. The following reagents were used in the experiments, having for their object the precipitation of one of the products of the dissolved active matter: Dilute ammonia, pyridine, fumaric acid, barium chloride followed by the addition of dilute sulphuric acid, and silver nitrate followed by the addition of dilute hydrochloric acid. The precipitates obtained were filtered off and dried on a hot aluminum plate and then tested for activity by the quadrant electrometer method, the Dolezalek form of instrument being used. Meanwhile the filtrates were evaporated to dryness in platinum dishes. The residues thus obtained were likewise tested for activity. Readings were then taken separately on the activity of both the precipitates and residues at suitable intervals during twenty-four to forty-eight hours. From the data thus obtained the curves of decay of the activity with the time were plotted.

A few experiments were also conducted with a view of effecting a separation of the two components simultaneously present on the platinum foils by direct treatment with some reagents. While a partial separation was obtained, our experiments in this direction are still incomplete.

Before giving the details of the separation one other general procedure must be added. In conducting the separations with ammonia, pyridine or fumaric acid, it was found necessary to add a drop or two of some compound which would form a precipitate with these reagents. A drop of a solution of ferric chloride was generally added. While a small quantity of activity was frequently obtained by simply adding the precitating reagent without the addition of ferric chloride, no uniform results could be obtained. By the addition of a trace of ferric chloride duplicate tests gave very closely agreeing results.

Experimental Results.—The addition of ammonia in slight excess to the hot nitric acid solution of the active matter dissolved

off the foils, and containing a trace of ferric chloride, gave a precipitate of ferric hydroxide that contained about 98 per cent. of the total activity and which decayed at the normal rate, falling to half value in eleven hours (curve A). Dilute ammonia then does not effect a separation of the two stages of the radio-active matter. The insolubility of Th A and Th B in dilute ammonia substantiates the result of Rutherford and Soddy[14] on the separation of Th X from solutions of thorium nitrate by means of this reagent. It will be recalled that these investigators succeeded in isolating from thorium nitrate solution by the addition of dilute ammonia in excess the radio-active type of matter Th X, which is responsible for the greater part of the activity exhibited by thorium compounds. In the precipitate of thorium hydroxide they found both Th A and Th B, thus leaving Th X in the residue obtained by evaporation of the solution.

Precipitation of Th B.—When pyridine is added in slight excess[15] to the hot nitric acid solution of Th A and Th B the precipitate obtained is very radio-active and its rate of decay very rapid. Its activity decreases approximately, according to an exponential law, falling to half value in about an hour, thus showing that pyridine makes a separation of the two components of the matter causing excited activity. (See curve B). Moreover, the filtrate, when evaporated to dryness rapidly, and the salts of pyridine expelled by heating, yields a residue which exhibits but slight activity at first, but rapidly increases, attaining a maximum value about four hours after precipitation, which in some experiments was fully five times the initial value. The curve showing the change in activity with the time closely resembles the theoretical curve A, plate 1. This curve represents the variation of the activity with the time when a quantity of Th A disintegrates, producing the radio-active product Th B with a half period of decay of fifty-five minutes. Curve A was plotted from values obtained for N_2 in the equation

$$N_2 = \frac{r_1 \, No}{r_2 - r_1} \left(e^{-r_1 t} - e^{-r_2 t} \right)$$ [16]

[14] Loc. cit.

[15] The addition of pyridine in considerable excess causes a precipitation of both Th A and Th B.

[16] See Rutherford, "Radio-activity," p. 371; also Stark, Jahrbuch der Radioaktivitat *1*, 4 (1904).

in which N_2 represents the number of atoms of Th B present at any time t; N_0 the number of atoms of Th A originally present; r_1 and r_2 are the radio-active constants of Th A and Th B, respectively, for which the Rutherford values $r_1 = .063$, and $r_2 = .75$, were used, t being expressed in hours. Since the activity of the products at any time depends solely upon the number of atoms of Th B undergoing change in unit time, the values of N_2 when multiplied by a constant give the arbitrary values for the activities plotted on the axis of ordinates in plate 1.

The separation of Th A and Th B by means of fumaric acid was conducted as follows: To the hot acid solution of the radio-active matter dissolved off the foils a few drops of ferric chloride were added, and then ammonia until the precipitate which formed just redissolved. Twenty cc. of a 1 per cent. solution of fumaric acid were then added, followed by sufficient ammonia to precipitate the iron completely, the final solution, however, still remaining acid. The slight precipitate was filtered off, rapidly dried on its filter, and the filtrate evaporated to dryness in a platinum dish. The activity of the precipitate and the filtrate was then measured separately at suitable intervals. The curves were practically identical with curves A and B. Fumaric acid, then, like pyridine, makes a separation of Th A and Th B. This behavior of Th A and Th B toward pyridine and fumaric acid confirms the results previously obtained by us in separating Th X from thorium nitrate solutions by means of these reagents.[17] It was found that the thorium precipitate contains Th B, but that Th A, being soluble in the above reagents, remained in the solution with Th X.

Precipitation of Th A.—When a few drops of barium chloride solution are added to a hot acid solution of Th A and Th B, obtained in the usual way, and a few drops of normal sulphuric acid added, and the precipitate filtered off, almost all the Th A was found in the precipitate, while the filtrate upon evaporation yielded a residue which had the rate of decay characteristic of Th B. Von Lerch,[18] in his study of the induced activity of thorium, performed the above experiment, but evidently failed to test the filtrate for activity. He states that the active precipitate had a normal rate of decay, but showed a slight initial rise characteristic of foils

[17] Loc. cit.
[18] Loc. cit., p. 756.

given a short exposure. In some of our experiments the activity of the precipitate increased tenfold in the course of three hours and then decayed at the normal rate. A fairly complete separation is therefore possible by this method.

The mere addition of a few drops of dilute sulphuric acid to the solution of Th A and Th B, free from barium chloride, fails to cause a precipitate of Th A. A good separation was also made by precipitating lead sulphate in the solution of Th A and Th B. The precipitation of silver chloride in the nitric acid solution of Th A and Th B, however, gave a precipitate practically free from both Th A and Th B. Moreover, by adding a little ferric chloride to the solution from which the silver chloride had been filtered, and then pyridine in slight excess, a precipitate was obtained containing the Th B, Th A remaining in solution. Pegram[19] precipitated silver chloride in a neutral solution of thorium nitrate and obtained a product containing Th B. As five grams of thorium nitrate were used, the active matter which adhered to the silver chloride may represent but a very small part of the total Th B which was present in the solution.

Effect of Lapse of Time.—The precipitations in all of our experiments described above were made immediately after the addition of the ferric chloride, barium chloride or silver nitrate. Inasmuch as the silver chloride precipitated in a nitric acid solution of Th A and Th B without lapse of time possessed exceedingly slight activity, some experiments were conducted to ascertain the effect of lapse of time upon the separations. Von Lerch in his paper is quite specific with regard to the time which elapsed before precipitation.

In one experiment the solution of Th A and Th B obtained by boiling the foils with 20 cc. of 3N nitric acid was made up to 20 cc. and divided into two equal parts. A few drops of silver nitrate solution were then added to each fraction. In one the silver chloride precipitate was formed immediately by adding a slight excess of hydrochloric acid. The other sample was set aside for three hours, when the silver was precipitated in the same manner. Both precipitates of silver chloride were practically inactive.

Similar experiments were also carried out with the other reagents employed. The products of the separations, however, were identical with those obtained by immediate precipitation.

[19] Loc. cit., p. 436.

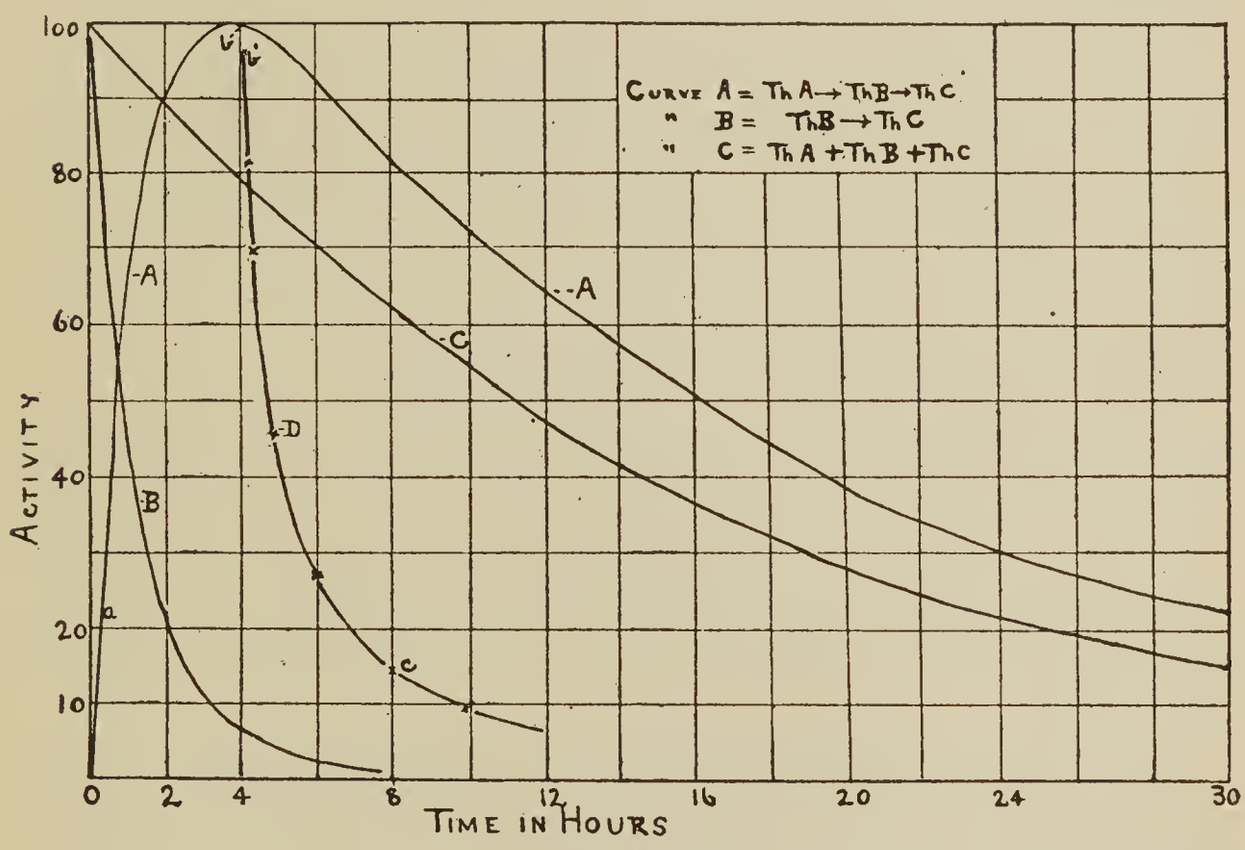
The separations were generally carried out in solutions of 10 cc. Equally good results, however, were obtained by means of pyridine in a sample of 2 cc., and in another of 100 cc. Further experiments on the effect of concentration were not performed.

In conducting the duplicate series of experiments in which hydrochloric acid solutions of Th A and Th B were used instead of nitric acid solutions, the residues obtained frequently proved quite inactive. The product Th A had apparently disappeared in the course of the separation. This loss of Th A was caused by finally heating the platinum dishes in which the filtrates were evaporated too strongly. The experiments of Miss Slater on the volatility of the active deposit clearly show that heating to redness for a few minutes readily volatilizes Th A. In any case, then, intense heating of the residues must be avoided. Some qualitative experiments which we performed, however, point toward a difference in volatility of the active residues obtained from the nitric and hydrochloric acid solutions. In one experiment the active nitric acid solution was divided into two equal parts and evaporated to dryness at 150° C. in platinum basins of approximately the same size and weight, and the activities measured. The dishes were then heated to redness for two and three minutes respectively with a triple Bunsen burner. Some Th A had been volatilized in this operation, but a considerable part of it still remained in each dish, as fully five hours elapsed before the activity decreased to half value. Less than 10 per cent. of Th B present was volatilized by the above treatment, as the residues were practically as active immediately after the heating as before. When a similar experiment was carried out with the residues from the hydrochloric acid solution the Th A product was entirely volatilized, while less than 6 per cent. of Th B was vaporized. The active residue decayed according to an exponential law, falling to half value in fifty-six minutes. Heating the hydrochloric acid present, then, to low redness for a few minutes leaves the pure Th B product.

Another experiment performed in this connection may be of interest: From the hydrochloric acid solution Th B was removed by precipitating it with pyridine. Four hours later, when the residue, Th A, had reached its maximum activity, it was heated to redness for two minutes and the decay of the activity with the time measured. The section a-b of curve A represents the increase

of activity of the Th A, while the section b′ c (Curve D) shows the decay of the activity of the residue left after it had been heated to redness for two minutes. The curve shows that fully 92 per cent. of Th A was volatilized.

Separation by Direct Treatment.—Some experiments were also conducted with a view of making a separation of the radio-active deposit on the foils by direct treatment. The solubility of the deposit in various reagents was extensively investigated by von Lerch.[20] He treated the deposit with hot and cold acids, bases and salt solutions, and with various organic solvents, and then determined the per cent. of activity dissolved off. His results, however, do not show whether a separation of the matter deposited on the foil ever occurred.



By boiling the foils for ten minutes in 40 per cent. alcoholic solution containing about 2 per cent. of fumaric acid the deposit left on the foils, instead of decreasing at the normal rate, half period of eleven hours, fell to half value in two hours. The residue obtained by evaporating the solution and igniting it showed an initial rise in activity, characteristic of Th A. Boiling with fumaric acid, then, in alcoholic solution makes a partial separation of the deposit, the product Th A being more readily removed. Further experiments on the removal of the active deposit with

[20] Loc. cit., p. 753.

aqueous solutions of fumaric acid and with pyridine solutions were conducted, but the results in hand are still too fragmentary for presentation. The separation of the components of the excited activity by direct treatment will be given further study.

Summary of Results.—(1) The experimental results obtained show that a separation of the products constituting the excited activity of thorium can be readily made by chemical methods.

(2) After removing the matter deposited on a negatively charged wire exposed for a long period to thorium emanation with acids, Th B may be obtained practically free from Th A with a precipitate of ferric hydroxide by means of pyridine or fumaric acid. The other component, Th A, remains in solution, and upon evaporation it remains as a residue. Ammonia does not make a separation.

(3) By precipitating barium sulphate (or lead sulphate) in a solution of Th A and Th B, Th A is found in the precipitate. The residue obtained by evaporating the filtrate decays in activity very rapidly, falling to half value in about fifty-six minutes—the characteristic rate of decay of Th B. The precipitation of silver chloride in an acid solution of Th A and Th B removes very little of either of the components from the solution.

(4) No differences were observed in conducting the separations immediately or after a lapse of time.

(5) The residue from the solution of Th A and Th B obtained by boiling the foils in hydrochloric acid is probably more readily volatilized than the deposit itself or the residue from the nitric acid solution.

(6) A partial separation of the two components of the excited activity may be made by direct treatment of the deposit with an alcohol-water solution of fumaric acid.

(7) The results of our experiments are readily explained by the theory of Rutherford as recently altered by him and Miss Slater. Our results clearly show that the first stage of the matter constituting the excited activity of thorium is an inactive product, Th A, with the slow rate of change, and that this produces the radio-active product Th B, which changes comparatively rapidly into the final product Th C.

(8) The results harmonize with the conclusion of Rutherford

and Soddy, that in the separation of Th X from ordinary thorium compounds, both Th A and Th B are precipitated with the thorium, and the result of the authors, that in the fumaric acid and pyridine separation of Th X the component Th B, of the excited activity, is simply present in the thorium precipitate.

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THE ELECTROLYTIC PREPARATION OF IODOFORM FROM ACETONE.

By G. A. Roush.

In 1884 E. Schering obtained a patent in Germany[1] for the preparation of iodoform by electrolysis, and in 1885 the same process was patented in the United States by Theodore Kempf[2]. The claim of this patent covers the electrolysis of any alkali or alkali earth iodid in the presence of alcohol, aldehyde, or acetone, but the specifications seems to indicate that in practice this was confined to the electrolysis of alcohol in a hot solution of potassium iodid and potassium carbonate.

This method has been studied repeatedly and conditions worked out by which good yields are obtained.[3]

Attempts to substitute acetone for alcohol in these methods were for some time unsuccessful. Elbs and Herz,[3] using an anode solution of 3-12 gms. sodium carbonate, 10-15 gms. potassium iodide, 93 cc. water and 27 cc. acetone at temperatures ranging from 20° to 40° C., and an anode density of 0.5-4.0 ampères per square decimeter, obtained no iodoform. They tried substituting sodium hydrate for the sodium carbonate in the above conditions, but the formation of iodoform was shown only by the odor of the solution, no solid being precipitated.

In 1901, Abbot,[4] in this laboratory obtained a current efficiency of 59.72 per cent. of iodoform from acetone by electrolysis in an alkaline solution, using the following conditions:

Current density; 1.35 ampères per sq. dm.

Temperature; 75° C.

Cathode solution: 10 per cent. sodium carbonate solution.

Anode solution: 6 gms. sodium carbonate, 10 gms. potassium iodid, 100 cc. water.

[1] D. R. P., 29.771, March 7, 1884.
[2] U. S. P., 372.940, July 28, 1885.
[3] Z. E., *4*, 113 (1897)
[4] Jour. Phys. Chem., 7, 84 (1903).

5.5 cc. acetone were added at the rate of 0.5 cc. every ten minutes during the electrolysis.

In 1903, Teeple[5] worked out conditions by which he obtained a current efficiency of 94.5 per cent. He used no diaphragm, a low anode density, high cathode density, kept the solution cool, well stirred and slightly *acid* in reaction.

Since the reaction which takes place continually sets free alkali he must add something to neutralize this. For this purpose he used carbon dioxid, hydrochloric acid, hydriodic acid and iodin. He prefers iodin, adding it gradually during the electrolysis in just sufficient quantity to keep the solution slightly colored. This iodin itself when added to the solution forms iodoform, thus making the method a combination of a chemical and an electrochemical process, and not purely electrochemical, although he calculates his yield as a purely electrolytic yield. Then he calculates that the amount of iodin to be added is just 50 per cent. of that freed by the current, but in his experimental work the actual amount used is 72 to 89 per cent.

Since the addition of iodin converts this into a combination of a chemical and an electrochemical method, means were sought by which this could be avoided and the alkali disposed of in a purely electrochemical way. The process described in the following pages was built up in the following way: The electrolysis of potassium iodid and acetone without a diaphragm gives the following reaction:

$$6KI + CH_3 \,.\, CO \,.\, CH_3 + 6H_2O = CHI_3 + CH_3 \\ COOK + 2KOH + 3H_2O + 6H.$$

This leaves in the solution two molecules of alkali for each molecule of iodoform produced. The electrolysis of a solution of potassium iodid and acetone with a diaphragm takes place according to the following equation:

$$CH_3 \,.\, CO \,.\, CH_3 + 6I + H_2O = CHI_3 + CH_3 \,.\, COOH + 3HI.$$

This leaves in the solution four molecules of acid for each molecule of iodoform produced.

Obviously, the thing to do was to combine these two electrolyses in such a way that the acid freed in the one should neutralize the alkali freed in the other, to bring about the conditions which

[5] J. A. C. S., *26*, 170 (1904).

Teeple's experiment showed to be the most favorable for the formation of iodoform; *i. e.*, a weakly acid solution.

On trial this method proved satisfactory, yields almost equal to the theoretical being obtained. It is probable that if a more accurate method for the determination of the iodoform had been available still better results would have been obtained.

Several forms of apparatus were tried, the following finally being adopted: The electrolyzing vessel was a crystallizing dish of 350 to 400 cc. capacity. The anode was a platinum crucible presenting about 15 to 20 square centimeters of electrode surface fixed on a shaft and rotated at a moderate speed. The rotating anode was used because it was the most efficient means of keeping the solution well stirred. Two cathodes were used. One was a platinum wire about 15 cm. long, 10 cm. of which were immersed in the electrolyte. The other cathode was of copper gauze of about 100 sq. cm. surface and was placed in a porous cup. For the sake of convenience we will designate these as the "regular" and "auxiliary" cathodes, respectively. Each cathode was connected to a separate resistance, so that the current could be regulated in one, independent of the other.

In this way the current entering the solution at the anode is divided into two parts, the first passing from the anode to the regular cathode, the second from the anode to the auxiliary cathode in the porous cup. The first will liberate two molecules of alkali for each molecule of iodoform it produces; the second will liberate four molecules of acid for each molecule of iodoform it produces. Theoretically, then, if the current in the auxiliary cathode is one-half the current in the regular cathode the solution would be kept neutral. In practice, however, the solution is to be kept slightly acid and the process does not give absolutely theoretical yields; hence the current in the auxiliary cathode is about two-thirds that in the regular cathode, varying with the conditions.

A copper voltameter was connected in series with the electrolytic cell to determine the amount of current used. The electrolyte was cooled by means of a current of cold water flowing through a glass coil immersed in the solution.

The amount of iodoform obtained was determined by filtering and drying, first in air, and then to a constant weight over phos-

phorus pent-oxid in a vacuum desiccator. The filter paper and residue were weighed in a stoppered weighing bottle to prevent the absorption of moisture during the weighing. The paper was then freed from iodoform, the last traces being dissolved off with a spray of alcohol or acetone from a wash bottle; it was then dried and weighed again as before. This care in drying and weighing was found necessary if accurate results were to be obtained.

The general conditions required were practically the same as found by Teeple, a cool, well-stirred solution, slightly acid in the reaction, and a low anode density.

Variations in the conditions within moderate limits had comparatively little effect on the yield. Changes of temperature seem to have the most effect. Any appreciable rise above 30 degrees centigrade lowered the yield, but an experiment run at 0° C. showed no appreciable increase in yield over that obtained at 20° C.

The following tables show the result of several of the electrolyses. In each case the potassium iodid was dissolved in 300 cc. water; 250 cc. of this solution along with the acetone were placed in the main electrolyzing vessel, the remaining 50 cc. being placed in the porous cup.

Table I shows the effect of a rise in temperature:

TABLE I.

No.	Gms. KI	c. c. Acetone	Reg. Cathode		Auxil. Cathode		Temp.	Time. Minutes	Gms. Cu Deposited	Theoret. Yield	Amount Obtained	Current Efficiency
			Curr'nt	Volt'ge	Curr'nt	Volt'ge						
1	20	3	1.3	5.9	0.9	7.3	18–19°	60	2.030	4.181g	4.041g	96.65%
2	20	3	1.35	7.8	0.85	7.5	21°	60	2.210	4.575	4.371	94.66
3	20	3	1.5	6.2	1.0	6.5	30–37°	60	2.663	5.485	5.126	93.81

Table II shows the effect of varying the amount of potassium iodid.

TABLE II.

No.	Gms. KI	c. c. Acetone	Reg. Cathode		Auxil. Cathode		Temp.	Time. Minutes	Gms Cu Deposited	Theoret. Yield	Amount Obtained	Current Efficiency
			Curr'nt	Volt'ge	Curr'nt	Volt'ge						
1	10	3	1.4	10.3	0.9	17.	15–16°	60	2.007	4.164g	3.935g	94.50%
2	20	3	1.3	5.9	0.9	7.3	18–19°	60	2.030	4 181	4.041	96.65
3	50	5	1.5	4.	1.0	5.2	12°	60	2.775	5.716	5.278	92.13

Table III shows the effect of varying the amount of acetone.

TABLE III.

No.	Gms. KI	c. c. Acetone	Reg. Cathode		Auxil. Cathode		Temp.	Time. Minutes	Gms. Cu Deposited	Theoret. Yield	Amount Obtained	Current Efficiency
			Curr'nt	Volt'ge	Curr'nt	Volt'ge						
1	20	0.5	1.3	6.5	0.9	9.7	15°	30	1.001	2 062	1.755	85.11%
2	20	1.0	1.3	· ·	0.9	· ·	16°	30	1.267	2.610	2.448	93.80
3	20	1.5	1.5	7.5	1.0	10	15°	30	1.353	2.787	2.660	95.44
4	20	3.	1.3	5.9	0.9	7.3	18–19°	60	2.030	4.181	4.041	96.65
5	20	5.	0.92	5.1	0.65	7.4	18°	70	2.260	4.661	4.434	95.01
6	20	10.	1.5	8.	1.0	12	15–16°	60	2.520	5.191	4.843	93.31

Table IV shows the results obtained from an electrolysis carried on for several hours. At the end of each hour the iodoform was filtered out and weighed. The solution was then heated to near boiling to drive out the remaining acetone, cooled, another portion of acetone added and electrolyzed another hour.

TABLE IV.

Hour No.	Gms. KI	c c. Acetone	Reg. Cathode		Auxil. Cathode		Temp.	Time	Gms. Cu Deposited	Theoret. Yield	Amount Obtained	Current Efficiency
			Curr'nt	Volt'ge	Curr'nt	Volt'ge						
1	50	5	1.5	4.4	1.	5.2	12°	1h.	2.775	5 716	5.278	92.33%
2	· ·	5	1.5-1.0	4.75–3	1.	5.3	12°	1 "	2.260	4.655	4.463	97.87
3	· ·	5	1.5	4.3	1-0.5	5.-3.5	10°	1 "	2.525	5.20	4 816	92.61
4	· ·	5	1.5-1.0	5 5	1.	6.3	11°	1 "	2.366	4.873	4.658	95.58
5	· ·	5	1.0	4.6	1.	5.1	12°	1 "	2.055	4.233	3.525	83.30

Two experiments were run for the acetone yield. (Table V.) The acetone yield was calculated on the basis that 0.147 gms. of

acetone should produce one gm. of iodoform. The same acetone was used in these experiments as in all others; it had been dried over calcium chloride and had a specific gravity 0.7858. These electrolyses were conducted the same as the others except that they were carried on until all of the acetone was used up.

TABLE V.

No.	Gms. KI	Gms. Acetone	Reg. Cathode		Auxil. Cathode		Temp.	Theoret. Yield	Amount Obtained	Acetone Yield
			Curr'nt	Volt'ge	Curr'nt	Volt'ge				
1	20	0.7858	1.5	6.8	1.0	6.5	15°	5.345 g	4.124	77.14%
2	20	1.5716	1.4	8.0	0.9	8.0	14°	10.69	7.748	72.48

According to these experiments the conditions which would give at the same time the highest current efficiency and the highest acetone yield, are as follows:

Electrolyte, 20 gms. KI;
300 cc. water;
1.5 cc. acetone;
Current, regular cathode, 1.5 ampères;
auxiliary cathode, 1.0 ampère;
Temperature, 15 to 18° C.

These conditions should give current efficiencies of about 95 per cent., and acetone yields of about 75 per cent.

In conclusion, I wish to thank Mr. F. C. Mathers and Mr. O. W. Brown for many valuable suggestions received during the course of this work.

Electrochemical Laboratory,
Indiana University.

DISCUSSION.

PRESIDENT BANCROFT: I wish to call attention to the very successful results that have been obtained in these last few years in the preparation of iodoform, bromoform, and chloroform from acetone. When experiments were first tried in Germany a number of years ago it was reported that it was possible to obtain only traces of these three substances. The current efficiency is now over 95 per cent. with iodoform and bromoform; 80 per cent. in the case of chloroform.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 20, 1905, President Bancroft in the Chair.

NOTE ON THE ELECTRICAL RESISTIVITY OF IRON AND OF STEEL AT HIGH TEMPERATURES.

By Gustave Gin.

The resistivities of the metals derived from iron have not been determined in the liquid state as they have in the solid.

The knowledge of the electrical resistance of these metals having been found of great importance for the study of my electric steel furnace, in which the Joule heat is produced in the metal itself while being refined, I have endeavored to measure the resistivity of the cast irons and steels, between their points of fusion and 1,800° C.

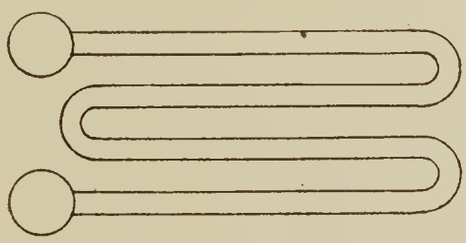

Fig. 1.

These results were effected in a furnace with a canal of great length and small section, forming an M, as in the accompanying sketch, and resembling a large incandescent lamp, the filament of which is constituted of a stream of fused metal. There is poured into the canal a volume, V, of iron, measured and weighed into the hopper and then the current is immediately turned on.

One alternator, or two, coupled in parallel, furnish the primary current at between 500 and 560 volts. A special transformer permits a reduction of the primary voltage in the following proportions:

	a	b	c	d	e	f
$\frac{E^2}{E^1} =$	$\frac{1}{45}$	$\frac{1}{36}$	$\frac{1}{30}$	$\frac{1}{22}$	$\frac{1}{18}$	$\frac{1}{15}$

In this manner by simultaneous variation of the system of transformation, and from the primary voltage, all the potential between 12 and 36 volts can be utilized. The intensity of the secondary current can be between 6,000 and 20,000 ampères.

The section of metal was at the moment of the introduction of the iron:

$$s = \frac{V}{l}$$

V being the volume of iron weighed in the hopper, and l the length of the canal.

This canal being moulded of chromite of iron of which the coefficient of expansion is negligible, we may consider its length and width as constant in the limits of temperature observed. The effect of the expansion of the metal results in an increase in the depth of the bath as represented,

$$h_{t_1} = h_{t_0} \left[1 + \alpha (t_1 - t_0)\right]$$

being the coefficient of the cubical expansion between t_0 and t_1 and t, which does not appear to have been found before, and will be found to approximate 13×10^{-5}, by direct measurement of the weight of metal in the crucible. This method of determination gives an uncertainty which is not perhaps appreciable, but which does not probably introduce an absolute error of more than 1-100 of the value of the resistivity at the high temperature observed.

These temperatures have been determined by means of a Fery optical pyrometer. The power, the tension and the bus bars of the furnace were measured by means of a watt meter of precision, by an ammeter and by a voltmeter. The hot filaments are measured with care.

At any temperature one has:

$$(1) \qquad W = EI \cos \varphi$$

$$(2) \qquad \frac{E}{I} = \sqrt{R^2 + \omega^2 L^2}$$

$$(3) \qquad \operatorname{tg} \varphi = \frac{\omega L}{R}$$

R being the contact resistance of the electrodes and the ohmic resistance of the bath.

It is admitted that the contact resistance should be independent of the temperature and proportional to I, therefore,

$$R_{t_I} = rI + \rho_t \frac{1}{s\,[1+\alpha\,(t_I - t_O)]} \qquad (4)$$

The volume, V^1, of liquid iron at a temperature of 1,280 degrees is first used, and W. E and I are determined. A volume V of the iron is made to flow and causes a variation of the constant of the current in such a manner so that I takes its initial value again.

The two equations,

$$\frac{E_I}{I} \cos \varphi_I = rI + \rho_{1280} \frac{1}{S}$$

$$\frac{E_2}{I} \cos \varphi_2 = rI + \rho_{1280} \frac{1}{s\,\frac{V-v}{V}}$$

are deduced, r and ρ_{1280}, $\cos \varphi_1$ and $\cos \varphi_2$ being furnished by the simultaneous reading of E_1, I, W_1 and of E_2, I, W_2.

The first experiments were made upon cast iron furnished by Messrs. Krupp, having the following composition:

Fe	93,032
Mn	2,752
C	3,337
Si	0,783
P	0,061
S	0,035

The resistivity of this iron has been found to be about 16 x 10^{-5} microhms centimeters for temperature between 1,280° C. and 1,340° C.

The author is continuing this study to determine the variations caused by temperature and the influence of impurities.

DISCUSSION.

Dr. Richards: This is probably the first published determination of a very important datum. The whole electrometallurgy of steel and calculations connected therewith will need such data in

the design of furnaces and in the running of them. I have not had the time since the report of the Canadian Commission came out to thoroughly analyze all of the data therein given; but I believe from the drawings and data which they have given, electrical and mechanical, and the analyses of the products, that probably there can be worked out from them the resistivity of the bath in a full state of transition from cast iron somewhat similar to this, perhaps, to pure iron; or, at least, the change from cast iron to a mixture having the composition of steel. It would be a good deal of work to do it; but I think that it can probably be worked out. As soon as the electrical manufacture of steel gets into regularly running, I do not doubt but that the electricians and metallurgists connected with it will be able, from actual practical experience, to find the resistance of different varieties of iron and steel at different temperatures, and thus fill up an enormous gap in the electrometallurgy of steel.

DISCUSSION.

(Communicated after adjournment.)

Mr. Carl Hering: Mr. Gin's figure for the resistivity of molten iron is evidently wrong, as molten iron would then have a conductivity 10,000 times as high as pure copper, which has a resistivity of 1.667 in terms of the same unit which he uses. This would evidently be absurd. From a determination made by W. Kohlrausch, I find that the resistivity of iron and cast steel at about a white heat, and therefore at almost the melting temperature, reduces to about 1.15 in ohm, meter, square millimeter units. Assuming that Mr. Gin meant to say "ohms," instead of "microhms," his figure would reduce to 1.6 in ohm, meter, square millimeter units. This would show that the resistivity when molten is slightly higher than the figure of Kohlrausch for just below the melting point, which is what might be expected. My contention that his figure is 1,000,000 times too small, or, in other words, that he meant to say "ohms" instead of "microhms," therefore, seems to be borne out by the Kohlrausch figures. It is of interest to notice that the specific resistance of molten iron is of the order of, and only slightly higher than, that of mercury at ordinary temperatures.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 20, 1905, President Bancroft in the Chair.

ON THE RADIO-ACTIVITY OF SOME NATURAL WATERS OF MISSOURI.

By Richard B. Moore and Herman Schlundt.

During the past year we have jointly tested about 20 samples of mineral waters of Missouri for their radio-active properties. The waters examined constitute but a relatively small proportion of the principal mineral waters, well known in different parts of the State. Inasmuch as the work cannot be continued jointly,[1] we have concluded to issue a preliminary report embodying the results obtained. The investigation, however, will be continued with a view of completing a general survey of the mineral waters of the State for their radio-active properties.

Method of Investigation.—The water samples were collected by the owners of the springs, or other reliable persons, according to a set of directions supplied by us. The samples were taken directly from the springs, or from the discharge pipe where the water was pumped, and at once placed in suitable stone jugs sent out from the laboratory. The collectors were especially cautioned against taking samples from reservoirs or overflow basins. The jugs were tightly corked, and the corks well coated with sealing-wax. The hermetically sealed samples were then shipped by express to the chemical laboratory of the university, where the tests for radio-activity were made. In three instances (samples numbered 16, 17 and 19) a second sample was collected independently by another person a day later. The close agreement of the values found for the activity of the duplicate samples was a source of gratification. In most instances a sample of the incrustations or deposits made by the waters was also supplied and tested for activity.

Upon arrival at the laboratory the water samples were immediately tested for their content of radium emanation by the fol-

[1] Now at Butler College, Indianapolis, Feb., 1906.

lowing method: A known volume—2.8 to 10.0 liters—of the water, to which a few cc. of caustic soda had been added to fix the carbon dioxide, was boiled for fifteen minutes, and the dissolved gases collected over water in a suitable gas burette.[2] The gas was then transferred to an air-tight electroscope, supplied with a reading microscope for noting the rate of fall of the leaf. The apparatus had previously been carefully standardized by means of a known quantity of emanation obtained from a sample of the mineral uraninite.

By the foregoing procedure the radium emanation present in the water is separated and stored for quantitative measurement. Readings on the rate of leak of the charged leaf were then taken. Owing to the activity induced on the walls of the electroscope the rate of fall of the leaf increases for fully three hours after the introduction of the gas, attaining a maximum value about 35 per cent. greater than the initial value. This maximum value was made the basis for determining the quantity of emanation present. Under these conditions the use of the electroscope for determining the quantity of radium emanation is fairly accurate. There is, however, one source of error which must be guarded against when the rate of fall of the leaf is rapid. For example, in connection with sample No. 16, in the table below, the leaf when first charged negatively at the time of maximum activity dropped through 60 divisions of the scale in one minute 28.4 seconds. Five minutes later, in one minute 23.6 seconds; again, after five minutes, in one minute 24.0 seconds. The leaf was kept charged negatively during the interval between the readings. The electroscope was then allowed to stand discharged for an hour, when readings were again taken, with similar results. The rate of fall of the leaf is thus about 5 per cent. faster after it has been kept charged for about five minutes than when first charged. The same difference in the rate of fall was observed when the leaf was kept positively charged. The observed increase in the rate of leak is probably to be ascribed to the concentration of an additional quantity of one of the products of the excited activity on the charged leaf system, this causing slightly more ionization in the immediate vicinity of the leaf. The introduction of error due to

[2] For a description of the apparatus employed, and the details of the method, the reader is referred to a former paper. Jour. Phys. Chem., 9, 320 (1905).

this behavior of our electroscope was eliminated by taking several readings at intervals of five minutes at the time of maximum activity, and neglecting the first reading in averaging.

In expressing the activity of the water samples, the standard proposed by Boltwood[3] was adopted. The activity of a given quantity of emanation is expressed in terms of uranium, and is based upon the existence of a constant ratio between the quantity of radium associated with uranium in natural minerals.[4] Our results on the activity of waters are expressed in terms of the unit representing the quantity of radium emanation associated with 1×10^{-4} grammes of uranium in a natural mineral.

The electroscopes used were standardized by means of a sample of uraninite which Dr. Boltwood kindly compared for us with his carefully standardized electroscope.

Results.—The samples of water tested are mostly mineral waters, but some deep-well waters used as water supplies are included. No attempts were made to test the waters for the presence of thorium emanation. The radio-active properties of the gases were found to be identical with those of the radium emanation, the activity falling to half value in approximately 3.8 days. No traces of radium salts were detected in any of the samples of water tested. In some cases several liters of the water were evaporated to dryness and the residue tested for activity by means of the quadrant electrometer method. But in most cases the samples were tested for radium salts by storing the water in tightly-corked vessels for a month, and then boiling off the gas a second time, and testing by the electroscopic method. When radium salts are present the water will regain its activity. In no case, however, did the second rate of leak differ appreciably from the normal air-leak, thus indicating the absence of even minute traces of radium salts in any of the waters examined. The deposits formed by the springs were also tested for activity by the electrometer method. The rate of leak, however, never exceeded the average air-leak sufficiently to give positive indications of the presence of any radio-active solids.

The quantitative results of the examination of the waters are given in the following table. The first column gives the laboratory

[3] Am. Jour. Sci. (4) *18*, 381 (1904).

[4] Boltwood, Am. Jour. Sci. (4) *18*, 97 (1904). Phil. Mag. (6), *9*, 599 (1905). McCoy, Ber. d. Deutsch. Chem. Gesell., *37*, 2641 (1904).

number, the second the name of the source, the third its location in the State—nearest post-office and county—and the last column the activity per liter of water in terms of the uranium standard, at the time the sample was collected. The decay in the activity of the samples during the interval between the time of collecting and the time of testing was corrected for by means of the formula $I_0 = I_t e^{rt}$, expressing the decay of the activity with the time. I_0 represents the initial activity, I_t the activity observed t hours after the water was collected, and r the radio-active constant of the radium emanation. The value of r used in the calculations was 0.0077, which is an approximate mean of the values found by several investigators. On an average about thirty hours elapsed between the collection of the sample and the test.

TABLE OF RESULTS.

Number	Name	Location	Activity $g \times 10^{-4}$ Ur.
1	Eldorado Springs	Eldorado Springs, Cedar Co.	1.4
2	Eldorado Deep Sulphur Well	" " " "	0.5
3	Cusenbury Spring	Independence, Jackson Co.	12.6
4	Plattsburg Spring	Plattsburg, Clinton Co. . .	3.7
5	Electric Spring	Warrensburg, Johnson Co.	2.25
6	Pertle Springs	" " "	2.9
7	Sweet Springs	Sweet Springs, Saline Co.	23.7
8	Akesion Water	" " " "	3.4
9	Boons Lick Spring	Fayette, Howard Co. . . .	4.6
10	The Artesian Well	Nevada, Vernon Co. . . .	4.5
11	Iron Spring	" " " . . .	2.0
12	White Sulphur Spring	" " " . . .	2.3
13	Alum Well	Versailles, Morgan Co. . .	0.8
14	Deep Well	Springfield, Green Co. . .	0.1
15	Greer Springs	Greer, Oregon Co.	0.4
16	Lake Spring	Kansas City (5 miles east)	48.2
17	University Deep Well	Columbia, Boone Co. . . .	1.5
18	Christian College Deep Well	" " " . . .	1.7
19	Rollins Spring	" " " . . .	4.5
20	City Deep Well	" " " . . .	0.25

The tabulated results show that marked variations exist in the activity of these cold waters. It is seen that the activity of the deep-well waters, as a rule, falls below that possessed by the spring waters. The list includes one or more waters from each of the principal classes of mineral waters enumerated by Dr. P.

Schweitzer in his extensive report on the mineral waters of Missouri.[5] The following classes of waters are represented in the table: (1) Muriatic or brines; (2) alkaline; (3) sulphatic; (4) chalybeate; (5) sulphur. Mineral analyses of nearly all of the waters examined were thus available. From the results in hand no connection between the mineral constituents and the activity could be noted. No mineral analysis of the most active water in the list, No. 16, Lake Spring, has been made. The second in activity, No. 7, Sweet Springs, is located in a region of saline waters. The water, however, contains far less sodium chloride than the salt springs of Saline and Howard Counties. Sample No. 9, Boons Lick Spring, contains fully 20 grammes of sodium chloride per liter, but it shows only one-fifth of the radium emanation found in Sweet Springs, No. 7, which contains about one-tenth the above amount of sodium chloride.

The results in the table are too few and scattered to establish any definite connection between the geological formation from which the springs issue and their radio-activity. Although the activity of the waters from the same locality shows an approximation in some instances, still in other cases we find marked differences in activity of springs in the same neighborhood—No. 7 and 8, for example. No relation appears to exist between the activity and the rate of flow.

Boltwood[6] has recently published the results of his tests on the radio-active properties of the waters of the Hot Springs Reservation, Arkansas. The results are expressed in terms of the uranium standard, thus enabling a direct comparison with our results. Of the 44 hot springs tested by Boltwood, five exceed in activity the most active sample, No. 16, given in the table above. The activities, however, vary remarkably, so that a considerable fraction of the hot springs falls below 10×10^{-4} grammes uranium per liter of water.

In conclusion, Boltwood directs attention to the necessity of making a quantitative test of the water from each spring in a given locality, in order to obtain a definite knowledge of the radio-active properties. Our results confirm this conclusion.

University of Missouri,
Columbia, Mo.

[5] Missouri Geological Survey, Vol. 3 (1892).
[6] Am. Jour. Sci., August, 1905.

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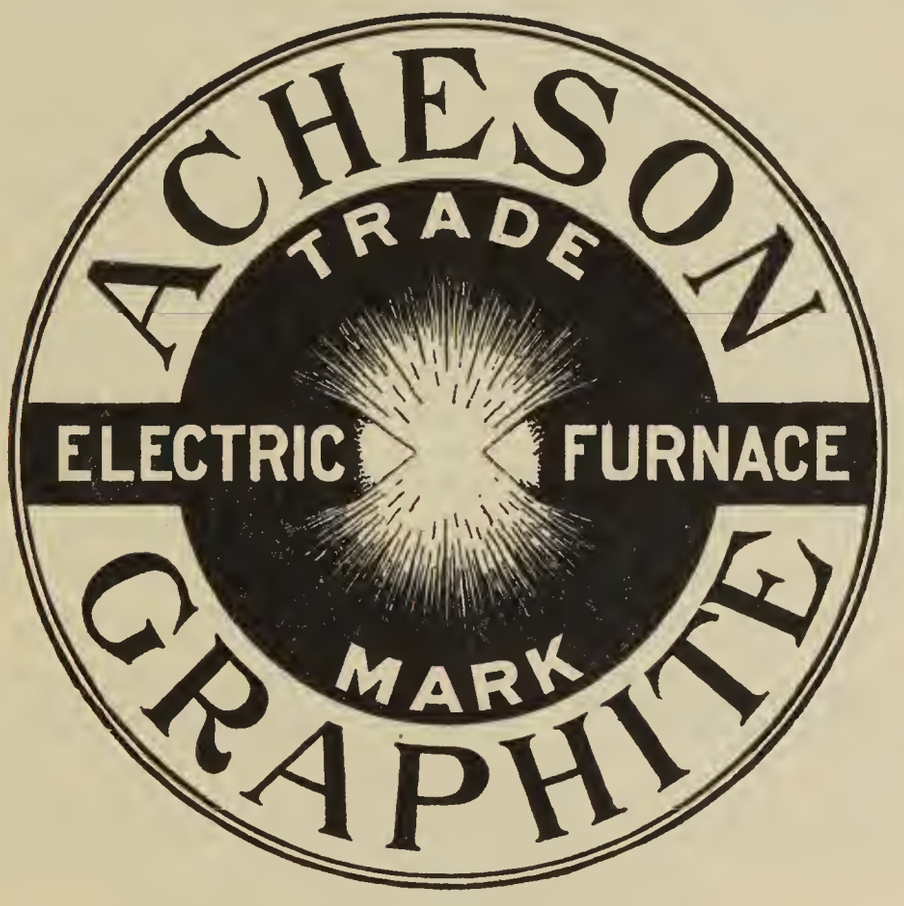

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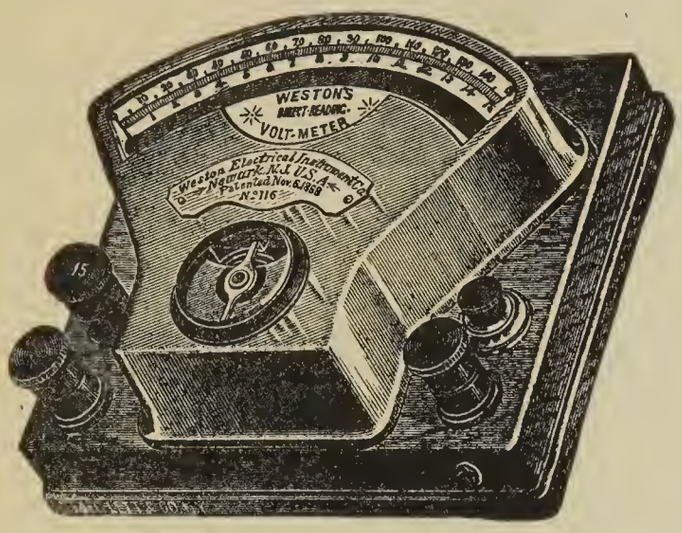

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